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**TRI-SERVICE
ENVIRONMENTAL TECHNOLOGY WORKSHOP**

***"Enhancing Readiness Through
Environmental Quality Technology"***

20-22 May 1996
Hershey, Pennsylvania

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U.S. ARMY ENVIRONMENTAL CENTER

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The U.S. Army Perspective

WORKSHOP THEME

“ENHANCING READINESS THROUGH ENVIRONMENTAL QUALITY TECHNOLOGY”

THE U.S. ARMY PERSPECTIVE

by COL DANIEL F. UYESUGI

Commander, U.S. Army Environmental Center

• *Readiness*

Readiness! The Army's ability to maintain a well-equipped, well-trained military is our number one priority. Environmental technology enhances readiness by preserving access to the air, land, and water necessary for training and testing. In addition, by maintaining a safe, healthful, and environmentally sound place to work, the Army maintains a high quality of life for the men and women who work and live on our military installations. Those men and women protect the national security. We, through our efforts, protect them.

This is accomplished in many ways. Through environmental restoration more land is available for training and living, through pollution prevention the costs of managing our hazardous wastes are reduced so that more funds are available for training, through compliance facilities continue to be available to test and maintain our forces, and through conservation the lands used for training retain their realistic nature and provide better environments for soldiers and their families.

But, accomplishing these things is also costly, time consuming and sometimes labor intensive. So, that is why there is a great need for new environmental technologies. Technologies that can make these accomplishments better, faster, cheaper, or safer.

- ***What's happening***

Let's look at the areas where technology is needed and some of the technologies that are being introduced.

⇒ ***Restoration***

Restoration is the largest area where technology can make a big dollar impact. Millions of acres of soil and millions of gallons of groundwater are contaminated through past practices. Contaminants include petroleum products, solvents, metals, explosives, chemical agents, and depleted uranium. In accordance with "Project Reliance" the Army focuses on explosives, site characterization, metals, and unexploded ordnance.

- * ***Explosives***

It was the U. S. Army Environmental Center that pioneered the use of incineration for explosive contaminated soil. It has been used to clean up soil contamination at Louisiana Army Ammunition Plant, Cornhusker Army Ammunition Plant, Savanna Depot Activity, and Alabama Army Ammunition Plant.

In recent years new technologies have been developed to deal with explosives. These have moved into the realm of biological degradation. The first to be demonstrated was composting. At Umatilla Army Depot Activity soils from a wash out pond were composted with local manures in static piles and by windrow. TNT was shown to be degraded and the resultant mixture was non-toxic. Based on this demonstration windrow composting was chosen to be the remedial action in the record of decision. The next was aerobic bioslurry both by itself and biosurfactant enhanced. The result was that this process can degrade explosive contamination and be an alternative to incineration. This process is being considered in the feasibility study of the Joliet Army Ammunition Plant.

While aerobic bioslurries have proven successful for the degradation of explosive contaminated soils anaerobic microbes work by a different metabolic process. This differing process is expected to aid in the degradation of more recalcitrant compounds such as RDX.

The use of plants to degrade explosives is presently getting greater attention. At present the most favorable technologies to remediate explosive contaminated soil are all ex-situ. No truly in-situ process has yet been found. But, phytoremediation could be that process. Many plants have been found that have a nitroreductase enzyme. These plants can degrade explosive contaminants. This is not just a process of plant uptake but one of actual degradation. The Army Environmental Center is presently working on a demonstration of phytoremediation in a wetland environment for explosive contaminated groundwater. But, this could be transferred directly to soils if proven successful.

* **Heavy Metals**

Heavy Metal soil contamination has also been a long standing problem. The two most used remedial actions at present are stabilization and dig and haul. While both technologies take the immediate problem away, they do not necessarily offer a permanent solution or an end to liability. So, now the use of soilwashing and leaching is being demonstrated. At the Twin Cities Army Ammunition Plant this process was used to remediate a lead contaminated site. The site was cleaned up and the lead was removed and recycled thus ending the chain of liability. While this process is effective for many metals it still has some disadvantages. The process is ex-situ, requires a large amount of equipment, and can be troubled by some metals such as mercury.

Up coming technologies for heavy metal soil contamination include phytoremediation and electrokinetics. Plants have also been shown to uptake metals. Therefore certain plant species can be grown in contaminated soil and after the growing season be cultivated, ashed, and the ash smelted. Electrokinetics is a process of placing an anode and a cathode in the soil, applying an electric current across the electrodes resulting in a current flow. Basically, by sending a current through the soil metal ions will migrate according to charge to the appropriate electrode and either be plated out onto the electrode or can be removed with the electrolyte solution produced. This has been pilot tested at Fort Polk where with the electrodes spaced six feet apart. 95% of the lead in the soil was removed. If demonstrated successfully at a large scale this process has the ability to be the in-situ answer to heavy metal contamination in many cases.

* **Other Contamination**

One other area of concern for the Army is Unexploded Ordnance. While not a soil contaminant in itself we do consider it a soil remediation problem especially at installations selected for closure. The Army has a very active program for unexploded ordnance detection and remediation. The Army Environmental Center

has set up a seeded test bed at Jefferson Proving Ground to allow primarily private sector companies to come in and demonstrate their capabilities in over-the-land and airborne unexploded ordnance detection.

In addition, the Center is also working on the development of better unexploded ordnance detection and remediation technologies such as the Subsurface Ordnance Characterization System (SOCS). SOCS is a test-bed system that simultaneously acquires data from a variety of mounted UXO detection sensors. The system's flexible, open architecture enables it to readily use different sensor technologies for UXO detection, identification, and localization.

The SOCS was successfully demonstrated at Tyndall AFB. The demo included a survey of a 1.5-acre test site that contained metal storage drums and buried inert ordnance. The results of the demo showed that the SOCS subsystems (e.g., navigation, autonomous vehicle control, sensors and data acquisition) could be successfully integrated and operated to characterize a site containing UXO.

* Site Characterization

Characterization of sites has been a long and costly activity. Technology has allowed us to achieve finer detail at contaminated sites, but at a cost. That cost often is more expensive equipment and longer analytical times.

Chromatography expanded our ability to look for suites of compounds. It also required skilled operators and large amounts of sample preparation. So, we began to look for analytical tools that could be used closer to the site of contamination. This led to some field kits. Field kits, as their name implies, were analytical tools that could be used in the field. The draw back was that most of these kits were only capable of gross measurements. Better tools were developed such as X-Ray Fluorescence. This technology has been of great benefit to quick field measurements. But, the application of this technology is limited.

The next generation of field portable analytical instrument is the SCAPS or Site Characterization and Analysis Penetrometer System. This system is a truck containing a hydraulic press that can push a probe into the soil. Based upon the sensor within the probe the SCAPS can measure what contaminants are present either in the soil or groundwater. Presently the most accepted sensor used by the SCAPS is one for petroleum products. Being demonstrated now

are additional sensors for volatile organic compounds, metals, and explosives.

Finally, the future could be the Ion-Trap Mass Spectrometer (ITMS). The ITMS is an analytical tool that is field portable, relatively easy to use, requires little sample preparation, and can provide near real time to real time monitoring of contaminants. Presently the ITMS is validated for the analysis of volatile organic compounds. Additional validation on other contaminants is continuing.

⇒ Pollution Prevention

There are many areas where the services can prevent or reduce pollution and many organizations are working on various problems unique to its service and of value to all services. Most pollution prevention activities focus on the industrial aspects but many military facilities have pollution prevention needs that are not industrially oriented. Some specific areas include wash racks and antifreeze recycling.

Washracks are used on everything from cars to tanks but often the existing racks are not designed to handle the kind of load the Army asks of them. The Army Environmental Center is demonstrating different washracks to determine the capabilities of differing systems so that recommendations can be made to installations on which type to purchase and use depending on the intended purpose.

A primary fluid used by the services is antifreeze. Millions of gallons of antifreeze are changed each year with the used antifreeze being disposed of. Technology has been developed to recycle antifreeze and to do it in such a way as to have the recycled product meet military specifications. The problem is that many facilities do not know this or use the recyclers incorrectly. The Center is taking GSA available recyclers and installing them in a few locations and developing installation, maintenance, and operational SOPs so that the facilities can use these recyclers properly and save money.

Pollution prevention can apply directly to range managers such as through lead build up on small arms ranges. With millions of rounds of small arms ammunition used each year in training exercises lead and lead run off can be a big problem. Methods to stabilize small arms range berms are presently being demonstrated to reduce erosion and run off and to better contain the lead bullets to prevent migration.

Closely related to lead on ranges is looking up the pipe, back to the ammunition itself. A project called "Green Ammunition" is

presently ongoing to make small arms ammunition more environmentally friendly. This project is looking at the lead bullet and the material in the primer. Substitutes are available for lead such as tungsten that can provide equal ballistics but not have the toxicity of lead. Also, new formulations are being developed for the primer that remove the hazardous material such as lead and actually provide greater power.

⇒ *Compliance*

Compliance with environmental laws such as the Clean Air Act and the Resource Conservation and Recovery Act can affect readiness. Military equipment must be protected from the elements and chemicals that they may come in contact with either during training or warfighting. The Army uses a compound called CARC or Chemical Agent Resistant Coating to protect its equipment. The present formulation of CARC is very much like paint and uses an organic base. This causes installations to spend a lot of time and funds on compliance with the Clean Air Act and volatile organic compound emission limitations and RCRA for the generation of hazardous waste that is associated with the protecting of the equipment. The Army is presently demonstrating a new formulation of CARC that is low volatile organic compound that will reduce many of the regulatory burdens.

Managing and monitoring hazardous materials and hazardous wastes is required by environmental regulations. Monitoring these items can also lead to better methods to store, distribute, and track generators of hazardous wastes. The Army is fielding a system called the Hazardous Substance Management System (HSMS) to track and report hazardous materials and wastes. This system was developed by the Navy and is being transitioned to the other services.

Biofiltration is another innovation coming to assist compliance. Presently, facilities that emit volatile organic or petroleum vapors must contain or destroy them. Technologies such as dry filters, water curtains, incinerators, and granular activated carbon are now used to do this work. A biofilter uses natural microbes to degrade the compounds thus disposing of the waste without the installation required to do further work. Biofilters have been proven for petroleum products and are now being demonstrated for volatile organic compounds.

One method a material can become a hazardous waste is by improper handling practices. When troops are in the field and training it is difficult to provide adequate and proper hazardous material storage and disbursement facilities. The Center is working to provide designs for this type of facility that can be

taken into the field and reduce the amount of hazardous waste generated.

⇒ *Conservation*

What environmental area could better focus on readiness than conservation. Conservation, by definition, is the controlled use and systematic protection of natural resources, as forests and waterways.

Dust Control during training operations is a major problem on military installations. Wheeled and tracked vehicles stir up huge amounts of fugitive dust as they move across dry, unsurfaced landscapes. Dust clouds limit soldiers' visibility, cause excessive wear and tear on equipment, create an air quality hazard, and can signal troop positions to enemy forces during training scenarios. A demonstration of a number of commercially available dust control agents is being conducted in large-scale field areas to determine the ability to reduce fugitive dust and compare cost and ease of use.

To maintain training lands in as realistic a setting as possible those lands must be rehabilitated after training is complete. To aid in this a program called VegSpec has been developed. In a collaborative effort between the Army and the Natural Resource Conservation Service, VegSpec provides land managers a method to select and combine plant species to revegetate damaged areas faster and with greater success. The program not only identifies the best species for the area but also aids the land manager by recommending seeding rates, dates for best growth, planting method, site preparation, cover requirements, and soil amendments.

The opposite problem also exists on military lands. The problem of how to deal with plant species that are noxious or nuisance. Presently pesticides are most often used to control these species. Pesticide use is in itself a problem and one the military is trying to reduce. So, a system to manage noxious and nuisance plants has been developed. This system contains information on a number of noxious and nuisance plant species and provides alternatives to pesticide usage such as biological controls that can be used. The system can also help with pesticide usage by identifying alternative pesticides or application practices.

Small arms range berm redesigns were discussed under pollution prevention but another method to reduce lead on ranges is the use of bullet traps. Bullet traps do as the name implies they trap bullets and contain them so that they do not get into the environment. A search has been made of existing bullet trap

designs and their application. The next step is to demonstrate the better designs at actual firing ranges.

- ***Cooperation and Coordination***

To better make environmental technologies applicable to readiness and other needs many partnerships are needed. The Army is cooperating with the Air Force, Navy, and other Federal agencies to leverage knowledge and ability. The Army is also making use of the Strategic Environmental Research and Development Program and the Environmental Security Technology Certification Program to leverage funds to ensure that good technologies get developed and demonstrated.

⇒ ***Tri-Service Environmental Centers Coordination Committee***

All of the military services have similar problems and each has a center to focus on these problems. To better aid in the transfer of information among the services the service center commanders got together and formed the Tri-Service Environmental Centers Coordination Committee. The purpose of the Committee is for the U. S. Army Environmental Center, U. S. Air Force Center of Environmental Excellence, and the U.S. Navy Facilities Engineering Service Center to exchange programmatic, regulatory, and technical information and develop and coordinate joint service activities relative to the programs, activities, matters, and issues of concern to the tri-service environmental centers that enhance the readiness posture of the services.

A charter has been executed by the Center Commanders and provide that each will exchange information and partner on research, development, demonstration, and transfer of environmental technologies and work together to gain acceptance of technologies by regulatory agencies among many other areas of interest to all of the services.

The committee meets at least three time a year and is already accomplishing many tri-service actions. Actions such as this tri-service environmental technology workshop, the development and acceptance of a tri-service "ecological risk assessment protocol" that will allow each service to conduct ecological risk assessments and present these as standard to the regulatory bodies, a tri-service pollution prevention handbook, regional office coordination, and partnered technology project proposals.

- ***Challenges***

⇒ ***Timely Availability***

Environmental technologies that are better, cheaper, faster, safer, or more acceptable are needed now not ten years from now. Good ideas that languish in the laboratory will be the death of themselves. With environmental funding going down and more and more sites entering the actual clean up phase if technologies are not available in the next two to maybe three years they will not be used or useful.

⇒ *Reliable Funding*

Second, because there are available technologies that need to get into the field from either Federal labs or the private sector there needs to be a reliable source of demonstration funding. The Army has not made available any research and development (6.4) money for the demonstration of environmental technologies. Some talk about SERDP (the Strategic Environmental Research and Development Program) and ESTCP (Environmental Security Technology Certification Program) as being the funding sources. But, this is not the case. SERDP is for basic and applied research not demonstration and is down to about 25% of what it once was. ESTCP while actually for the demonstration of environmental technologies may not exist next year with all of the budget cutbacks. Also, with the number of congressional earmarks the amount of funding available for demonstrations that the services actually need is small. Compounded by the fact that a small amount of funding has to be spread among the services and the length of time it takes to get the money to the actual executors this program does not begin to cover the need.

• *Summary*

Readiness and environmental protection are not competitors they are complimentary. As the Army strives to maintain the readiness of our warfighters they can also conserve the environment and benefit from environmental regulation. But, new tools and methods will be needed in order to continue to provide realistic training. The Army is working on these issues and in many areas we are succeeding. The direct benefits to the Army and all of the military will be better training facilities and realism, more training opportunities, and reduced life cycle operating and maintenance costs.

WEAPONS SYSTEMS

MINERAL ACID PURIFICATION OPPORTUNITIES

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ABSTRACT

Extending the life of mineral acid baths is environmentally and economically attractive. There are technologies currently available that can offer these benefits. Two such technologies are diffusion dialysis and acid sorption. These two competing technologies were objectively evaluated using bench scale equipment to compare their ability to remove metal contaminants and recover free acid from a contaminated mineral acid bath.

This comparison provides some criteria for evaluation of each technology when applied to the recovery of hydrochloric acid (HCl) from iron (Fe) contaminated hydrochloric acid solutions. The solutions prepared in the laboratory for these tests closely approximate actual spent hydrochloric acid activation and cleaning baths.

While the results indicate that both technologies are effective in recovering free acid and removing iron from the test solutions, there are distinct differences between the two. The diffusion dialysis system achieved acid recoveries averaging 97% and iron rejection averaging 86%. Acid sorption achieved acid recovery and iron removal efficiencies of approximately 96% and 45%, respectively.

Conclusions for diffusion dialysis are:

- the diffusion dialysis system has a higher HCl recovery efficiency per gram of acid fed to it, but because of the degree of osmosis occurring within the membrane stack during these tests, the diffusate acid concentration is approximately 55 - 60% of the feed acid concentration,
- the diffusion dialysis system achieves greater percent rejection of the contaminant metal in the feed; approximately 52% higher than acid sorption in this case (osmosis acts to increase metal rejection)
- fresh make up acid will be required when processing a work tank with a diffusion dialysis system (quantity will be dependent on system performance and the ability to minimize osmosis),

Conclusions for acid sorption are:

- the acid sorption system has a lower HCl recovery efficiency per gram of acid fed to it, but because of how it was operated, the recovered acid product is actually more concentrated than the feed,
- the acid sorption system will eliminate the need for make up acid into the working tank (the recovered acid product will actually need diluted prior to re-introduction to the working tank),
- average metal removal efficiency range from the feed to product stream is 38 - 44%

These technologies may be operated in batch or continuous mode. Diffusion dialysis is more suited for continuous mode, due to the time required to reach equilibrium. Acid sorption has more flexibility to operate efficiently in either mode. Choosing a technology and mode of operation will be dependent on

purity requirements of the bath, the bath volume to be processed, and the required flow rate. Operating costs for each system will be minimal due to their simplicity. Equipment costs and product purity requirements will govern technology selection. These factors will vary from one application to another. Applications that require high bath purity and a low feed processing rate may be best suited for diffusion dialysis. Conversely, applications requiring higher feed processing rates, and less stringent bath purity may be more conducive to acid sorption. Correct technology selection must be based on the actual application and will vary based on the mineral acid and metal contaminant concentrations.

Overall, both technologies provide viable at-source opportunities for recovering acid and minimizing waste handling costs, while maintaining higher quality baths and increased productivity.

1.0 INTRODUCTION

Mineral acids are used in many applications throughout industry. Some of the more common applications include cleaning, activating, anodizing, and pickling of raw metal stock and finished metal parts. Mineral acids are also used for the same processes in repair facilities. For example, metal parts are processed in mineral acid baths after initial forming and manufacturing steps, after cleaning and prior to painting and plating operations. During use, the baths become contaminated with dissolved metal ions. Eventually, the concentrations of the dissolved metals reach a level that renders the bath depleted and no longer capable of performing properly. Present methods for maintaining acceptable metal contaminant levels consist of partial or complete bath dumps. This method of operation requires complete fresh acid bath make up and treatment or offsite disposal of the dumped solution. Due to their wide use, industry is recognizing the economic and environmental benefits of extending the life of mineral acid baths. There are technologies currently available that can offer these benefits. Two of these technologies are diffusion dialysis and acid sorption. These two competing technologies were evaluated to objectively compare their ability to remove metal contaminants and recover free acid from a contaminated mineral acid bath. Implementing such a technology offers the potential to minimize fresh acid bath make up costs and reduce treatment and/or offsite disposal costs. Maintaining consistently higher quality baths can also contribute to consistently higher quality product at lower costs.

2.0 DIFFUSION DIALYSIS THEORY

Diffusion Dialysis is a membrane separation technology that relies solely on concentration gradient between a dilute solution (deionized water) and a concentrated solution (contaminated acid) to effect transport of ions. The two solutions are physically separated by an anion permeable and ion selective membrane. The membrane acts as the barrier at which ion transport (migration) occurs. Ion migration across the membrane occurs due to the high concentration difference between the solute (acid) and the solvent (D.I. water). The anion permeable membrane allows negatively charged acid ions to migrate through the membrane, while rejecting the positively charged metal ions. In order to maintain electroneutrality, and because they are very small, positively charged hydrogen ions also migrate through the membrane.

A typical diffusion dialysis system is comprised of a stack of membranes with interior channeling to effectively increase surface area and promote ion migration. The membranes are usually formed from copolymers of polystyrene and divinylbenzene. Operation involves passing the feed acid stream into the bottom of the membrane stack and deionized water into the top of the stack. A countercurrent flow arrangement maintains the most effective concentration gradient throughout the entire membrane stack. Acid feed and deionized water head tanks are physically located above the membrane stack. This allows the head pressure from the height difference to push the fluid through the membrane stack. Flow control

devices such as metering pumps or control valves are typically placed on the lines exiting the stack. These flow control devices are used to optimize the flow rate of the exiting streams and improve the ion migration process. The two streams exiting the process are referred to as diffusate, the acid rich and metal depleted solution, and dialysate, the depleted acid and metal rich solution. Figure 1 schematically illustrates a typical diffusion dialysis system.

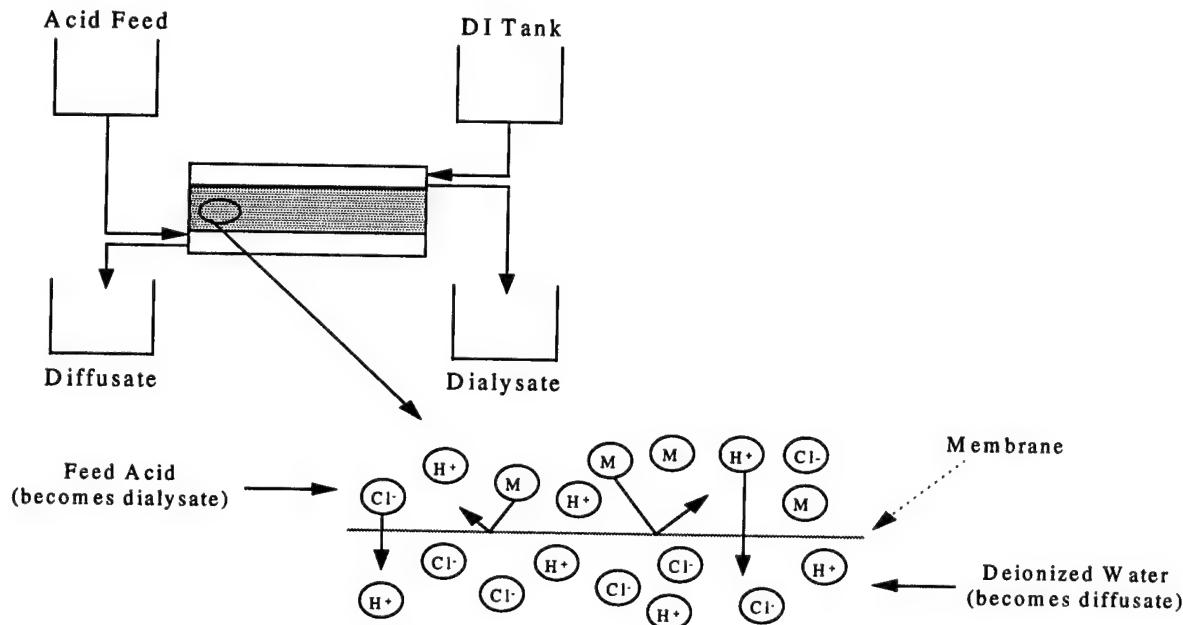


Figure 1. Diffusion Dialysis System

2.1 Process Considerations

Several physical variables affect the performance of a diffusion dialysis system. These variables are acid and metal concentrations, solution flow rates, and osmosis within the membrane stack.

Acid and metal concentrations in the feed acid greatly affect the efficiency of acid recovery and metal rejection. A feed solution with high acid concentration will typically give better percent acid recovery in the diffusate when compared to one with low acid concentration. This is due to the greater concentration gradient across the membrane. Conversely, a high concentration of metal in the feed acid tends to allow greater leakage of metal into the diffusate.

The flow rates of diffusate and dialysate must remain relatively constant. The ratio of flow rates between the two streams can range from 0.8 to 1.2. Varying the ratio of flow rates allows the operator to tailor the process to achieve different results. For example, operating the system with the diffusate flow rate higher than the dialysate flow rate will provide lower acid recovery and higher metal rejection. Operation with the diffusate flow rate lower than the dialysate flow rate will provide a higher acid recovery and lower metal rejection. This characteristic of the diffusion dialysis process allows flexibility to tailor the process to various applications.

Diffusion dialysis systems typically require 24 to 36 hours to reach equilibrium after initial start up. This is due to the relatively slow nature of the concentration gradient driven process and the corresponding long residence time requirement of the solution in the membrane stack. During the time required to reach

equilibrium the diffusate produced may not be acceptable for reuse. Periodic sampling (once every 8 to 12 hours during start-up) and analysis of the diffusate and dialysate is necessary to trend performance and note that equilibrium has been reached. Sampling and analysis frequency can be reduced once the process has reached equilibrium.

Actual operation of a diffusion dialysis system is relatively simple and does not require much operator intervention. Main requirements for proper operation are maintaining constant diffusate and dialysate flows and recording the volume of waste acid and deionized water fed to the system. It is very easy to study a diffusion dialysis system prior to observing one in operation and assume that the volume of feed acid fed to the system equals the volume of dialysate produced, or that the deionized water volume fed to the system equals the volume of diffusate produced. This, in fact, is not the case. The reason for this discrepancy is osmosis within the membrane stack. Just as the concentration gradient causes acid to migrate through the membrane into the deionized water, the same gradient causes osmosis, or water migrating through the membrane into the acid. The effect of osmosis, in this case, is that the feed acid stream becomes diluted. The effect of osmosis can be minimized by adjustment of the diffusate and dialysate flow rates. However, in addition to flow rates, acid and metal concentrations play a role in osmosis. The operator must be aware of the potential for osmosis to occur and react accordingly. For example, a mass balance on the process may indicate that the system is recovering 95% of the acid feed. However, due to osmosis, the acid concentration in the diffusate will not be 95% of the original feed acid concentration.

2.2 Performance Evaluation

Diffusion dialysis system performance is determined through calculations using recorded flow rates and concentrations of the feed acid, diffusate, and dialysate streams. The two main performance indicators are percent acid recovery and percent metal rejection in the diffusate. Percent acid recovery is determined using mathematical equation 2.2.1. Percent metal rejection is determined using mathematical equation 2.2.2.

$$\% \text{ Acid Recovery} = 100 \times (F_{\text{diff}} \times \text{Acid}_{\text{diff}}) / [(F_{\text{diff}} \times \text{Acid}_{\text{diff}}) + (F_{\text{dial}} \times \text{Acid}_{\text{dial}})] \quad (\text{Eq. 2.2.1})$$

Where,

- F_{diff} = Diffusate flow rate
- $\text{Acid}_{\text{diff}}$ = Diffusate acid concentration
- F_{dial} = Dialysate flow rate
- $\text{Acid}_{\text{dial}}$ = Dialysate acid concentration

$$\% \text{ Iron Rejection} = 100 \times (F_{\text{dial}} \times \text{Met}_{\text{dial}}) / [(F_{\text{diff}} \times \text{Met}_{\text{diff}}) + (F_{\text{dial}} \times \text{Met}_{\text{dial}})] \quad (\text{Eq. 2.2.2})$$

Where,

- F_{dial} = Dialysate flow rate
- Met_{diff} = Dialysate metal concentration
- F_{diff} = Diffusate flow rate
- Met_{dial} = Diffusate metal concentration

3.0 ACID SORPTION THEORY

Acid sorption is a chemical technology designed to separate dissolved metals and complexed acid from free acid. Ion exchange resin is utilized to adsorb free acid while allowing complexed acid and dissolved metals to pass. The main steps in purifying metal contaminated mineral acid with this system are a

loading step in which the free acid is adsorbed onto the resin, and a regeneration step in which water is passed over the loaded resin to pull off the free acid.

The process sequence for the equipment used for this demonstration/validation involves four steps. The four steps are:

- Step 1 - Volume V_b of feed acid is pumped from the feed acid reservoir through the resin column, displacing the water resident on the column from the previous cycle. The free acid is adsorbed by the resin as it passes through the column and the displaced water returns to the water reservoir.
- Step 2 - Volume V_a of feed acid is pumped into the column displacing volume V_b which contains the metal salts and any residual acid. This step produces the by-product.
- Step 3 - Volume V_c of water flows countercurrently into the column and displaces unprocessed acid back to the acid reservoir.
- Step 4 - Volume V_d of water, also flowing countercurrently, displaces the acid rich product to the recovered acid storage tank. This cycle of four steps is repeated in approximately five minute intervals.

Figure 2 schematically illustrates the system used for this work.

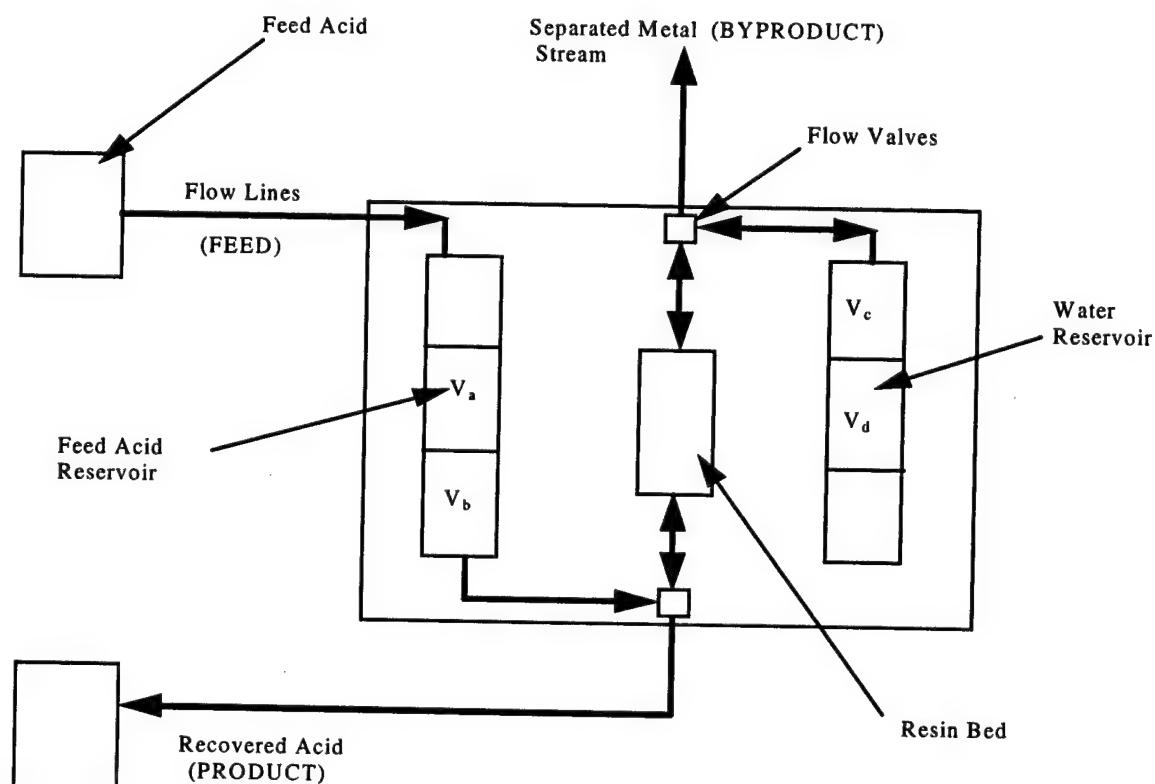


Figure 2. Schematic of Acid Sorption System

3.1 Process Considerations

The resin column used for testing was 2 inches in diameter and 12 inches long. Column diameter will be increased for larger scale applications requiring higher resin volume. The resin used in the acid sorption system is proprietary.

The volumes and flow rates for each process step must be set according to the manufacturers instructions. Varying the flow rates of acid feed and water feed streams affects the recovery and removal efficiencies to a small degree.

Time to achieve equilibrium for this system is approximately one half hour. After initial start up the recovered acid and by-product streams are sampled and analyzed for free acid content. Equilibrium is considered to be reached when the variation of acid concentration varies by only five to ten percent between sequential cycles. The system was then allowed to run for four or five cycles to collect representative samples for analysis and comparison.

3.2 Performance Evaluation

Acid sorption system performance is determined by performing calculations using the data from each process cycle. The two main performance indicators are acid recovery efficiency and metal removal efficiency. Acid recovery efficiency is determined using mathematical equation 3.2.1. Metal removal efficiency is determined using mathematical equation 3.2.2.

$$A_{\text{eff}} (\%) = [(A_{\text{prod}} \times \text{Prod}_{\text{vol}}) / (A_{\text{feed}} \times \text{Feed}_{\text{vol}})] \times 100 \quad (\text{Eq. 3.2.1})$$

Where,

- A_{eff} = Acid recovery efficiency
- A_{prod} = Product stream acid concentration
- Prod_{vol} = Product volume collected during cycle
- A_{feed} = Feed solution acid concentration
- Feed_{vol} = Feed solution volume processed during cycle

$$\text{Met}_{\text{eff}} (\%) = [(\text{Met}_{\text{prod}} \times \text{Prod}_{\text{vol}}) / (\text{Met}_{\text{feed}} \times \text{Feed}_{\text{vol}})] \times 100 \quad (\text{Eq. 3.2.1})$$

Where,

- Met_{eff} = Metal recovery efficiency
- Met_{prod} = Product stream metal concentration
- Prod_{vol} = Product volume collected during cycle
- Met_{feed} = Feed solution metal concentration
- Feed_{vol} = Feed solution volume processed during cycle

4.0 EXPERIMENTAL APPROACH

All experimentation and analysis was performed by Concurrent Technologies Corporation (CTC). The purpose of this experiment was to objectively evaluate and compare the performance and applicability of diffusion dialysis and acid sorption for purifying mineral acids.

Bench scale equipment was used to perform all testing. The time required to reach equilibrium for the diffusion dialysis system and the overall time constraints for performing the tests, allowed for only two trials for each technology to be performed. Solutions believed to be representative of those commonly used in industry were selected as the test solutions. The test solutions consisted of two hydrochloric acid (HCl) solutions at different acid concentrations contaminated with different concentrations of iron (Fe). They were to represent a typical HCl steel cleaning bath and an HCl steel activation bath. Synthetic solutions were formulated on-site to represent these typical baths. Table 1 illustrates the concentrations used for testing.

TABLE 1. TEST SOLUTION CONCENTRATIONS

Trial #	Solution	Diffusion Dialysis		Acid Sorption	
		HCl (g/l)	Fe (g/l)	HCl (g/l)	Fe (g/l)
1	Cleaning	45.5	37.4	45.3	38.1
2	Activating	131	66.1	136	68.4

4.1 Diffusion Dialysis Set-up

Each trial for the diffusion dialysis system was run continuously for approximately 104 hours. Flow rates were selected such that the dialysate flow was faster than the diffusate flow. The ratio of dialysate to diffusate flow was kept in the range of 1.1 to 1.2. The flow rates were maintained constant throughout the trial. This was done in attempt to achieve higher acid recovery while possibly sacrificing metal rejection performance. Again, due to time constraints, it should be noted that the flow rates were not optimized. Measurement of flow was performed using a calibrated stopwatch and a graduated cylinder. To assure reasonable accuracy in measurement, the flow rate data used was an average of three measurements taken sequentially.

For material balance purposes, the volume of feed acid and deionized water fed to the system was measured. This was done by measuring the liquid height in the head tank and calculating the volume using the known length and width dimensions.

Grab samples of diffusate and dialysate were taken twice daily for analysis. Flow rates were also measured at this time. The feed acid and deionized water head tanks were sampled only once a day. These samples were analyzed for free acid and total iron content using titration standard ASTM E 224, and Inductively Coupled Plasma (ICP) standard EPA 200.7, respectively. To ensure the integrity of the data, all samples were analyzed using the appropriate QA/QC procedures.

4.2 Acid Sorption Set-up

The bench scale acid sorption equipment was run at the manufacturers recommended flow rates. These process settings were stated as being the optimum conditions to run for the given feed solutions. Flow rates were obtained by measuring product and by-product volumes and dividing them by the cycle time, which was measured using a calibrated stopwatch.

Grab samples of the recovered acid and by product stream were taken after start-up to note when equilibrium was reached. Once equilibrium was achieved, four samples from sequential cycles were collected for laboratory analysis. Feed, recovered acid, and by-product were analyzed for free acid and total iron content using titration standard ASTM E 224, and ICP standard EPA 200.7, respectively. All necessary QA/QC procedures were followed to ensure data integrity.

5.0 RESULTS

The raw data was collected and reduced using the equations described above. The results were then presented in graphical formats to clearly convey and compare the performance of the two systems. Performance results for each technology are compiled and given below.

5.1 Diffusion Dialysis Results

The percent acid recovery and percent iron rejection results varied slightly throughout the time of each trial. These minor variations were judged to be insignificant (+/- 0.5 - 1.5% variation). Trial 1 had an average acid recovery of 97% and an average iron rejection of 89%. Trial 2 had average acid recovery of 98% and average iron rejection of 83%. Figure 5.1.1 illustrates the trend of percent acid recovery for the entire time of each trial. Figure 5.1.2 illustrates the trend of percent iron rejection for the entire time of each trial.

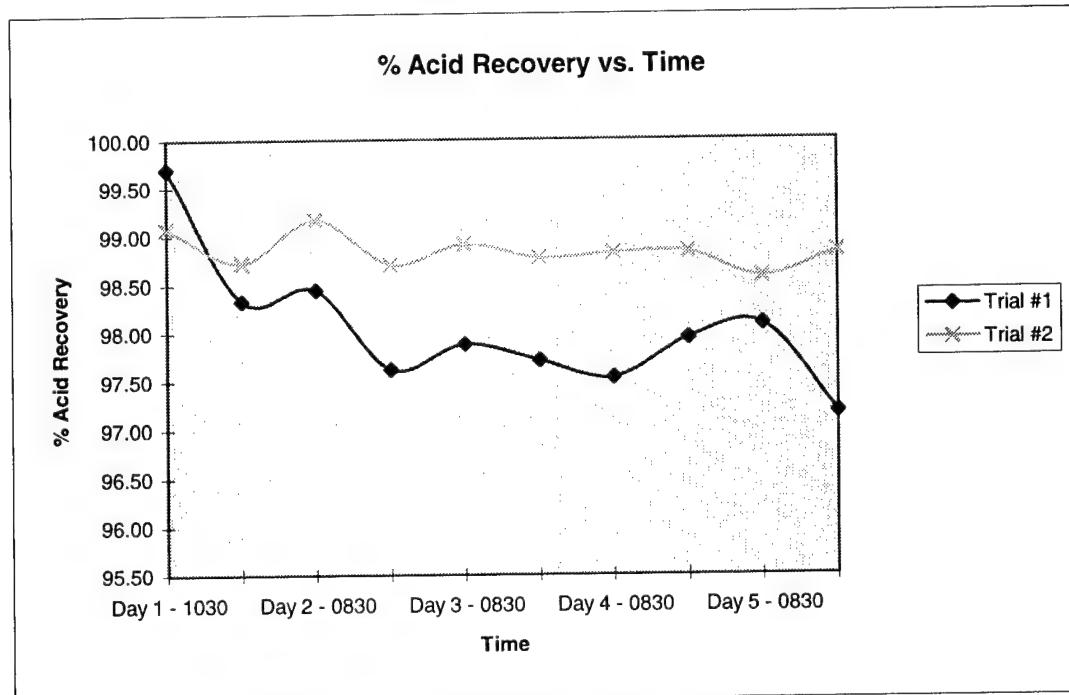


Figure 5.1.1. Percent acid recovery for each trial

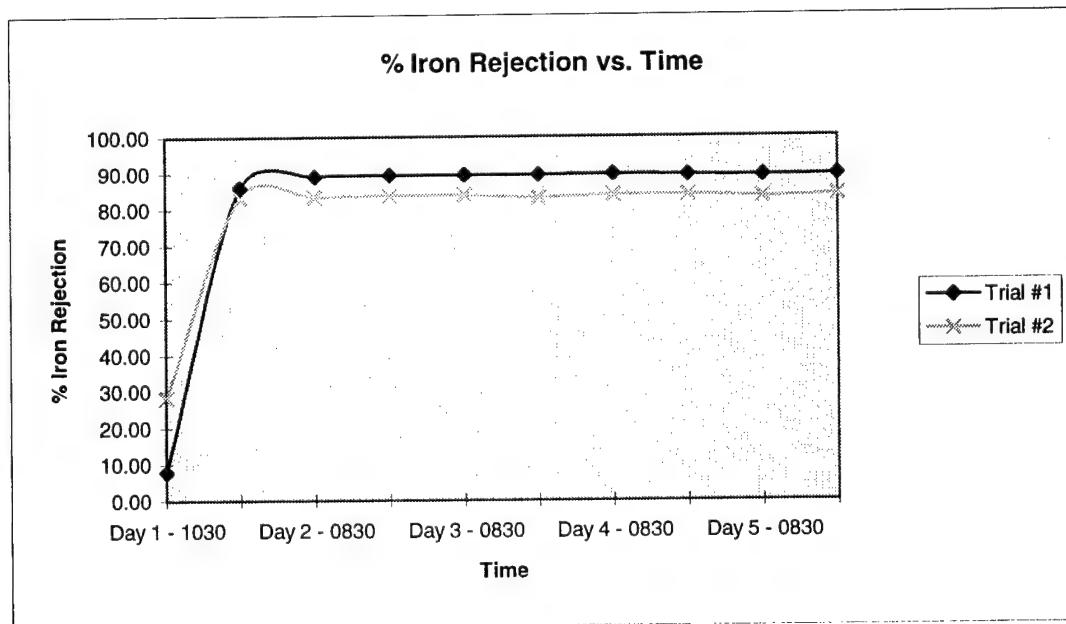


Figure 5.1.2. Percent iron rejection for each trial

After performing the overall material balance for each trial it is evident that osmosis was substantially diluting the feed acid and causing the concentration of acid in the diffusate to be significantly lower than that of the feed. Based on calculated percent acid recoveries for trials one and two, the concentrations of acid in the diffusate were expected to be approximately 44 g/l and 128 g/l, respectively. Actual concentrations of the diffusate streams were approximately half of the acid feed stream. Table 2 presents these results and illustrates the differences in acid concentration between the feed and diffusate. Again, it is important to note that flow rates were not optimized in these tests. Varying flow rates will minimize the dilution of the feed acid caused by osmosis. This can effect can be manipulated advantageously depending on the desired results in actual operation (i.e. recovered acid purity vs. metal rejection).

TABLE 2. DIFFUSION DIALYSIS FEED AND DIFFUSATE COMPARISON

Trial #	HCl in Feed (g/l)	HCl in Diffusate (g/l)	% Dilution
1	45.5	26.9	~41
2	131	73.9	~44

5.2 Acid Sorption Results

Results for the acid sorption trials presented here are the mathematical average of four samples taken from sequential cycles after reaching equilibrium. The average acid recovery and iron removal efficiencies are given in Table 3.

TABLE 3. AVERAGE ACID SORPTION EFFICIENCIES

Trial #	HCl Recovery Efficiency (%)	Fe Removal Efficiency (%)
1	97.7	47.0
2	94.3	41.6

Observing the acid concentration in the feed acid and the recovered acid product indicates that the product has a higher acid concentration than the feed. This occurs because the quantity of water used to recover the acid was less than the quantity of acid fed to the column. Therefore, the concentration increase is not an indication that acid is produced, but simply that the same quantity of acid is present in a smaller volume of liquid. The comparison of feed acid to recovered acid product is given in Table 4. Of special interest is the fact that although the recovered acid was more concentrated than that of the diffusion dialysis, the recovered acid was less pure than the diffusion dialysis recovered acid. A comparison of iron in the feed and product streams for both technologies is given in Table 5.

TABLE 4. ACID SORPTION FEED AND PRODUCT COMPARISON

Trial #	HCl in Feed (g/l)	HCl in Diffusate (g/l)	% Concentration
1	45.3	47.2	~104
2	136	145	~107

TABLE 5. PRODUCT STREAM PURITY COMPARISON

Trial #	Diffusion Dialysis		Acid Sorption	
	Fe in feed (g/l)	Fe in diffusate (g/l)	Fe in feed (g/l)	Fe in product (g/l)
1	37.4	2.2	38.1	21.7
2	66.1	5.9	68.4	42.6

CONCLUSIONS

It should be noted that the results presented here are only based on two trials. Also, due to time constraints, the diffusion dialysis system was not operated at optimized process settings. Therefore, the performance of the diffusion dialysis system may have considerable room for improvement if optimized settings were achieved.

Conclusions for diffusion dialysis are:

- the diffusion dialysis system has a higher HCl recovery efficiency per gram of acid fed to it, but because of the degree of osmosis occurring within the membrane stack in this instance, the diffusate acid concentration is approximately only 55 - 60% of the feed acid concentration,
- the diffusion dialysis system achieves greater percent rejection of the contaminant metal in the feed; approximately 52% higher than acid sorption in this case (osmosis acts to increase metal rejection)
- fresh make up acid will be required when processing a work tank with a diffusion dialysis system (quantity will be dependent on system performance and the ability to minimize osmosis),

Conclusions for acid sorption are:

- the acid sorption system has a lower HCl recovery efficiency per gram of acid fed to it, but because of how it was operated, the recovered acid product is actually more concentrated than the feed,
- the acid sorption system will eliminate the need for make up acid into the working tank (the recovered acid product will actually need diluted prior to re-introduction to the working tank),
- average metal removal efficiency range from the feed to product stream is 38 - 44%

These technologies may be operated in batch or continuous mode. Diffusion dialysis is more suited for continuous mode, due to the time required to reach equilibrium. Acid sorption has more flexibility to operate efficiently in either mode. Choosing a technology and mode of operation will be dependent on purity requirements of the bath, the bath volume to be processed, and the required flow rate. Operating costs for each system will be minimal due to their simplicity. Equipment costs and product purity requirements will govern technology selection. These factors will vary from one application to another. Applications that require high bath purity and a low feed processing rate may be best suited for diffusion dialysis. Conversely, applications requiring higher feed processing rates, and less stringent bath purity may be more conducive to acid sorption. Correct technology selection must be based on the actual application and will vary based on the mineral acid and metal contaminant concentrations.

Overall, both technologies provide viable at-source opportunities for recovering acid and minimizing waste handling costs, while maintaining higher quality baths and increased productivity.

APPLICATION OF MID-INFRARED SPECTROSCOPY TO THE IDENTIFICATION OF MATERIALS AND TO THE DETERMINATION OF SURFACE COATINGS

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ABSTRACT

A small user friendly, light-weight, field hardened, computer controlled device for performing infrared spectroscopic analysis, with high sensitivity of trace contamination on surfaces, has recently been defined by Lockheed Martin Energy Systems, Inc. The National Aeronautics and Space Administration at Marshall Space Flight Center, Alabama (NASA/MSFC) initiated a development contract to field a production model of this device with Surface Optics Corporation, San Diego, California in order to certify the sandblasted inner surface of solid rocket motor casings to be free of both hydrocarbon grease and silicone oils at levels approaching 1 milligram per square foot. Through contracts with Lockheed Martin Energy Systems, Inc., the Army acquired a prototype of this instrument, which was used for optimizing the performance with respect to detecting trace organic contamination on sandblasted metal surfaces. That prototype has since been upgraded to incorporate the refinements discovered in its use, and is presently being field tested by the Army at the Corpus Christi Army Depot (CCAD). Referred to as a surface inspection machine-infrared (SIMIR or SOC 400), this device employs a miniature Fourier transform Infrared spectrometer (FTIRS) with very efficient diffuse reflectance optics to provide reflectance spectra of surfaces measured relative to some reference surface. These spectra are capable of yielding qualitative and quantitative chemical information from a host of surfaces that has imminently practical applications in the determination of surface identification, contamination, and degradation. The performance of the SIMIR and its initial applications to surface inspection at CCAD that include sandblasted metal surfaces, as well as, detection of contamination on other metal finishes such as black oxide finished steel.

1. INTRODUCTION

Alternative industrial cleaning processes are increasingly being implemented throughout the Department of Defense due to the environmental banning of halogenated cleaning solvents. However, the uncertainty associated with the effectiveness of the new cleaning processes often requires that the level of cleaning be verified prior to the continuation of manufacturing processes such as painting or surface plating. Many of

^aManaged for the U. S. Department of Energy by Lockheed Martin Energy Systems, Inc. Under Contract No. DE-AC05-84OR21400

these tests are time consuming, do not provide definitive results, and will not quantify levels of cleanliness to a high level of accuracy.

Diffuse reflectance mid-infrared spectroscopy is a very useful tool for the inspection of surfaces in manufacturing applications,¹ particularly those related to the cleaning of metals. In collaboration with Harrick Scientific Corporation, remote sensing infrared accessories have been developed and field demonstrated to be practical means of surface inspection for organic contamination on metals^{2,3}, lithium hydroxide on lithium hydride⁴, and heat damage to graphite-epoxy laminates⁵. The method is also applicable to identifying organic solids; and for characterizing textiles, paper, wood, coal, and adhesives^{1,6}. Recent collaboration between the Lockheed Martin Energy Systems, Inc., NASA/MSFC, the Army, and Surface Optics Corporation has extended these developments to the extent that practical, user-friendly, very-sensitive infrared surface inspection machines are in service at sites of these collaborators, and are available in the market place⁶.

The Surface Optics Corporation SOC 400 Surface Inspection Machine / InfraRed (SIMIR)⁶ was designed to meet a NASA requirement that the sandblasted inner surface of solid rocket motor casings be free of both hydrocarbon grease and silicone oils at levels approaching 1 milligram per square foot (~ 10 nm films). Through contracts with Lockheed Martin Energy Systems, Inc., the Army acquired a prototype of this instrument, which was used for optimizing the performance with respect to detecting trace organic contamination on sandblasted metal surfaces. That instrument has since been upgraded to incorporate the refinements discovered in its early use. This SOC 400 is presently being field tested by the Army at the Corpus Christi Army Depot (CCAD), where infrared surface inspection is being extended to surfaces that are more challenging than sandblasted metals. This paper describes this hand-held (or remotely positioned) Fourier transform infrared spectrometer (FTIRS) that uses diffuse reflectance optics to interrogate surfaces. The performance is demonstrated in terms of the signal-to-noise of the instrument (i.e., the sensitivity of the SOC 400 in spectrometric units) when used to inspect highly reflective sandblasted surfaces, the fingerprints of contaminants (various oils and soap residues) on metals at approximately the 100 mg per square foot level, and to the inspection of machined, black oxide finished steel gear components where the analysis is complicated by the lower light scattering ability of machined surfaces and the presence of spectral features due to the black oxide film.

2. THE SOC 400 SIMIR

The Surface Optics Corporation SOC 400 Surface Inspection Machine / InfraRed (SIMIR)⁶ shown in Figure 1 weighs less than 8 Kg and may be operated at any orientation. The SIMIR is based on barrel ellipse diffuse reflectance optics having a focal point located in the plane of an opening in the face plate of the instrument. This barrel ellipse optical configuration is shown in Figure 2. The system is supported by either 12 VDC or 120 VAC and a computer using MIDAC GRAMS/386. At this workshop, the SOC 400 was operated from a 90 MHz Pentium Computer and, interchangeably, with a 486 laptop computer. The SOC 400 operates at <40 W, slightly less than the power requirements for the laptop computer. This "point-and-shoot" type of instrument allows rapid in-field analyses to be made with sensitivity comparable to laboratory FTIRS. Dedicated scanning and collection routines, and the robust characteristics of the barrel ellipse focal point with respect to sample positioning substantially enhance the utility of the SOC 400. The capability for having the spectrometer software instruct positioning devices in a noncontact mode is sometimes utilized^{3,6}, usually with dramatic increases in productivity and utility.

The key to the performance of the SIMIR is the integration of an intense source, very efficient collection of diffusely scattered light, and an infrared light detector having very high signal-to-noise, the achievement of which, for a given collection time interval is the best method for defining performance in a FTIRS. That

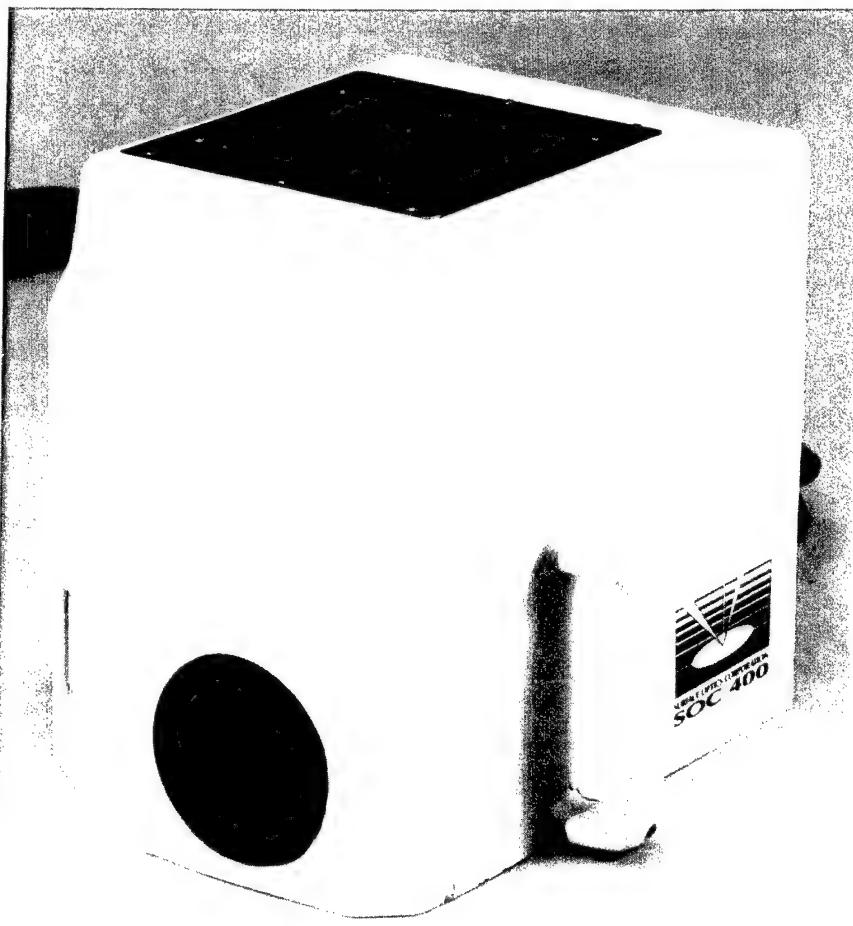


Figure 1. The SOC 400 Surface Inspection Machine/InfraRed (SIMIR). The sampling point of the diffuse reflectance optics is at the center of the 85-mm diameter dark circle.

function is described in Figure 3. The operating system may also be customized using MIDAC/Grams386/Array Basic or MIDAC Visual Basic software for dedicated inspection operations. This is done to make the inspection operation user friendly, hardened against accidental loss of data and changes in operational parameters, to introduce dedicated post processing of data, and to instruct external devices by serial communications to reposition the specimen and execute other operations.

3. SURFACE INSPECTION OF METALS

The SOC 400 operates in a similar fashion to most laboratory FTIRs, a characteristic that makes its operation and data evaluation very familiar to most experimental chemists. The difference with respect to laboratory instruments is that aligning accessories and waiting for the spectrometer to purge no longer exist. The SOC 400 and the specimen surface are brought into appropriate proximity, made easy by the contact face plate, and the spectrum is collected while observing the spectrum develop in nearly real time (1.3 s phase lag). With respect to observing stains on metals, a fortuitous property of sandblasted metals (the archtypical surface for adhesive bonding to metals) is that applying a nonvolatile oil or powder to sandblasted metal substrates, followed by vigorous scrubbing of the substrate with a simple tissue to remove as much residue as possible, leaves an optimum residue for producing a library spectrum.

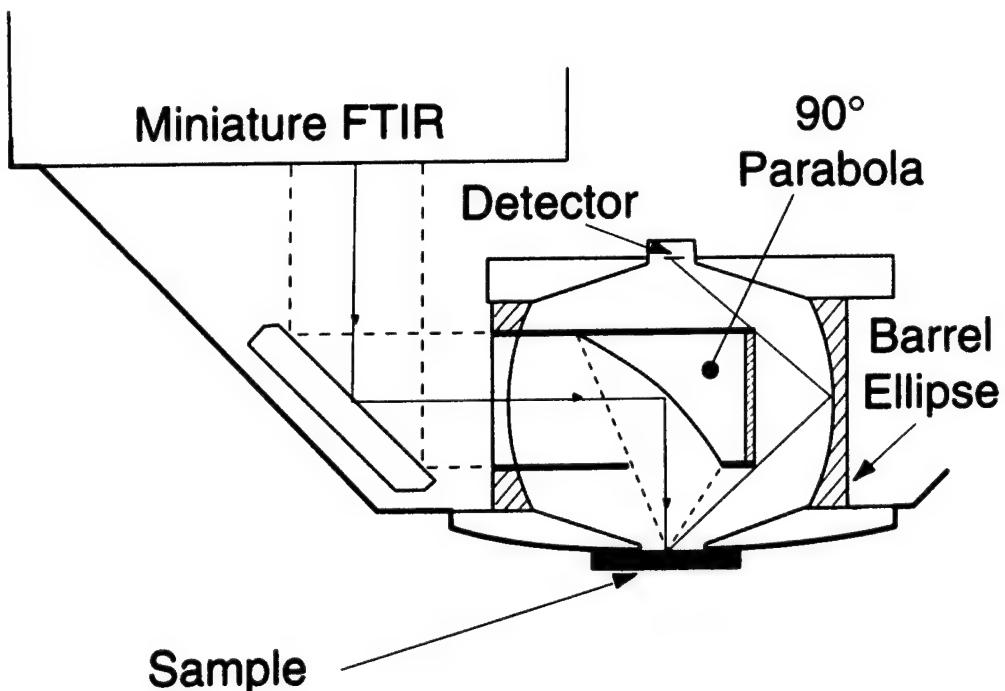


Figure 2. The barrel ellipse diffuse reflectance collection optics in the SOC 400. The collimated beam from the FTIR is focused on the sample by a parabolic mirror. Light scattered by the sample at angles greater than the angles of incidence are focused on the detector by the barrel shaped elliptical mirror.

Now that the acquisition of spectra has been greatly simplified, the focus turns to the hard part. An infrared spectrum is a measure of light absorption in one substrate relative to another, usually called the reference or background. With respect to certifying the cleanliness of metals, the inspector must know that the reference spectrum is clean within the detection limits of the method. Contamination must not be transferred from one substrate to another, an event that is easily avoided by operating in a noncontact mode. In the process of cleaning metals, this is the technique intensive process of keeping a clean part clean.

Sandblasted gold is the optimum substrate material for metal cleanliness studies because gold is easily cleaned. Gold it can be cleaned with very harsh chemical methods. Gold is one of the most reflective of metals and displays no features related to oxide films. Thus, sandblasted gold returns to the infrared detector a true representation of the spectral distribution of the incident beam. Sandblasted aluminum is also a good substrate, but the aluminum oxide film can significantly contribute to the spectral features. Highly anodized aluminum strongly absorbs over much of the mid infrared spectral range. Sandblasted stainless is also a good substrate in that it is very durable and cleanable. It does contribute some oxide film features to the spectra. Again the emphasis is on this form of surface inspection as a comparative technique suggesting that the background spectrum for surface cleanliness approximate as closely as possible the clean substrate of the surface being analyzed.

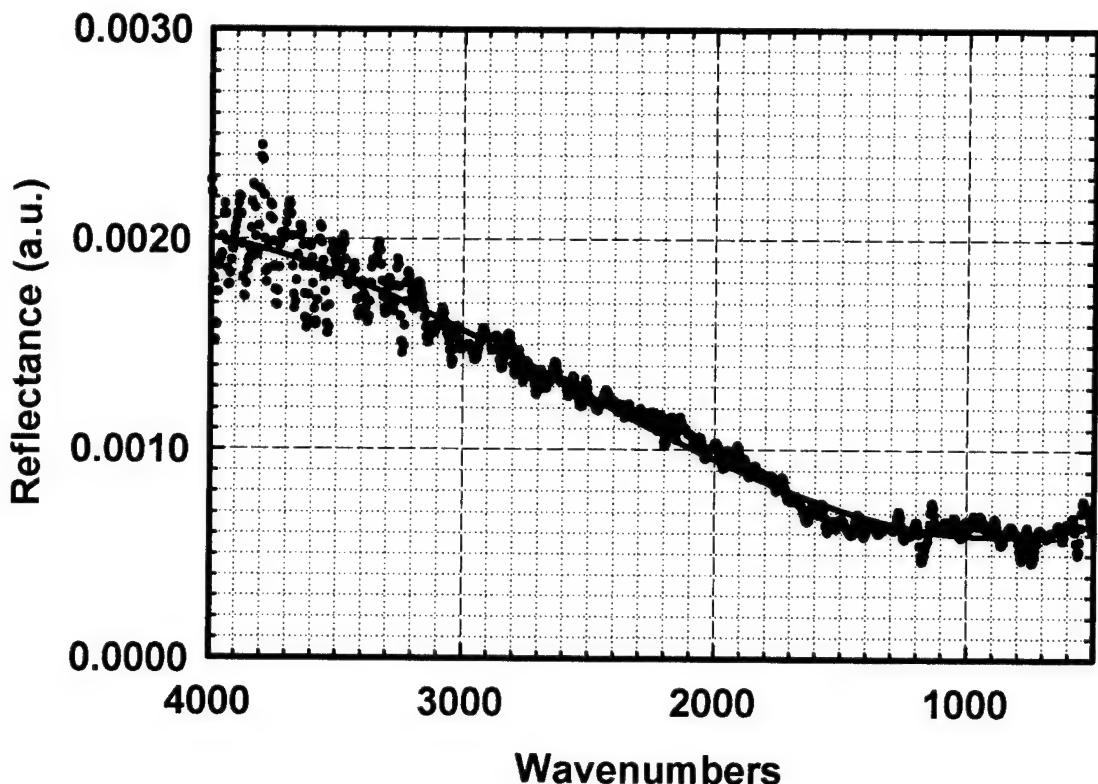


Figure 3. An infrared spectrum obtained from a sandblasted gold specimen using 16 cm^{-1} resolution, 2 times zero filling, and 48 coadded scans (1 min.) referenced to the same specimen background spectrum collected for 256 coadded scans. The graph shows the noise in the spectrum relative to a fourth order polynomial curve fit to the data.

3.1 LIBRARY SPECTRA

Figure 4 shows library-type spectra of common classes of contaminants found in cleaning operations. The mineral oil spectrum is pharmaceutical grade light mineral oil. The strongest band is due to the stretching frequencies of aliphatic hydrocarbons and is the general signature of contamination by organic materials. The remaining two weaker bands define the stain as a simple hydrocarbon. Many commercial greases and oils fit this pattern, but they may be complicated by additives that may uniquely identify the source of the contamination. Safflower oil is a household cooking oil (a triglyceride) that is distinguished by the carbonyl bands at 1735 cm^{-1} and additional bands at lower wavenumbers. Like the aliphatic hydrocarbon stretching band, this carbonyl band is another excellent indication of organic contamination. This band alone is not sufficient to identify the stain as a vegetable oil. The small band at 3011 cm^{-1} indicates that it is an unsaturated oil. Silicone oil (Dow Corning DC200-5cps) is easily distinguished from mineral and vegetable oils by the shape of the band near 3000 cm^{-1} (Silicone has only methyl hydrogens), the Si-C band at 1265 cm^{-1} , and the Si-O bands near and below 1000 cm^{-1} . The Hershey cocoa butter soap is an example of a soap made by the saponification of triglycerides, resembling the safflower oil spectrum with the exception that the carbonyl band is shifted to lower wavenumbers because it is now a carboxylic acid. The broad bands near 3400 cm^{-1} seen to some extent in all these spectra results from hydroxyl species, usually due to water in or under the films or due to alcohols in the stain. A general rule of thumb is that an 0.1 a.u. response corresponds to a film thickness for the stain of approximately one micron (100 milligrams per square foot) although the surface texture may affect the exact value of the stain film thickness considerably. Comparing Figure 3 (the system signal-to-noise) the common stains in Figure 4, shows that

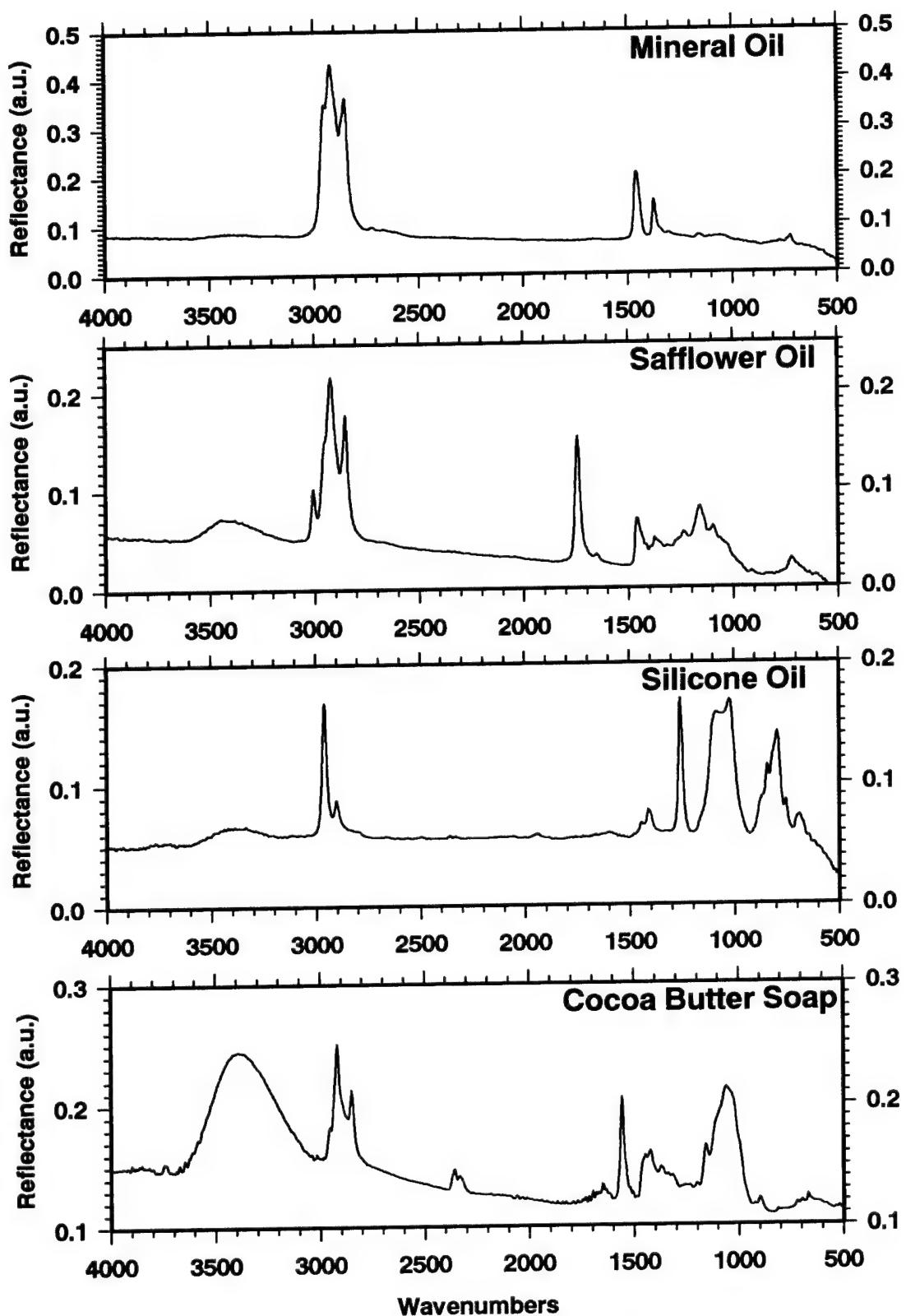


Figure 4. Library spectra obtained using smear stains on sandblasted steel, showing the unique patterns of common surface contaminants. These spectra represent film thickness on the order of one micron (100 milligram per square foot).

it is possible to detect an infrared response for contamination that is 1000 times less than the thickness of commonly occurring stains. Very elegant statistical algorithms now exist to search out and identify these library spectra with little operator intervention.

Figure 5 shows three spectra of suspected contaminants for which a chemical analysis was not immediately available. The rinse water concentrate is from a rinse bath that was thought to be approaching its limit for accrued detergent. The concentrate was placed on sandblasted aluminum and allowed to evaporate. The fingerprint spectrum was obtained from a fingerprint smudge applied to sandblasted aluminum. The unknown oil was an oil droplet found on a black oxide steel gear component. It was smudged onto sandblasted aluminum to make this library spectrum. The oil is clearly an aliphatic hydrocarbon ester with

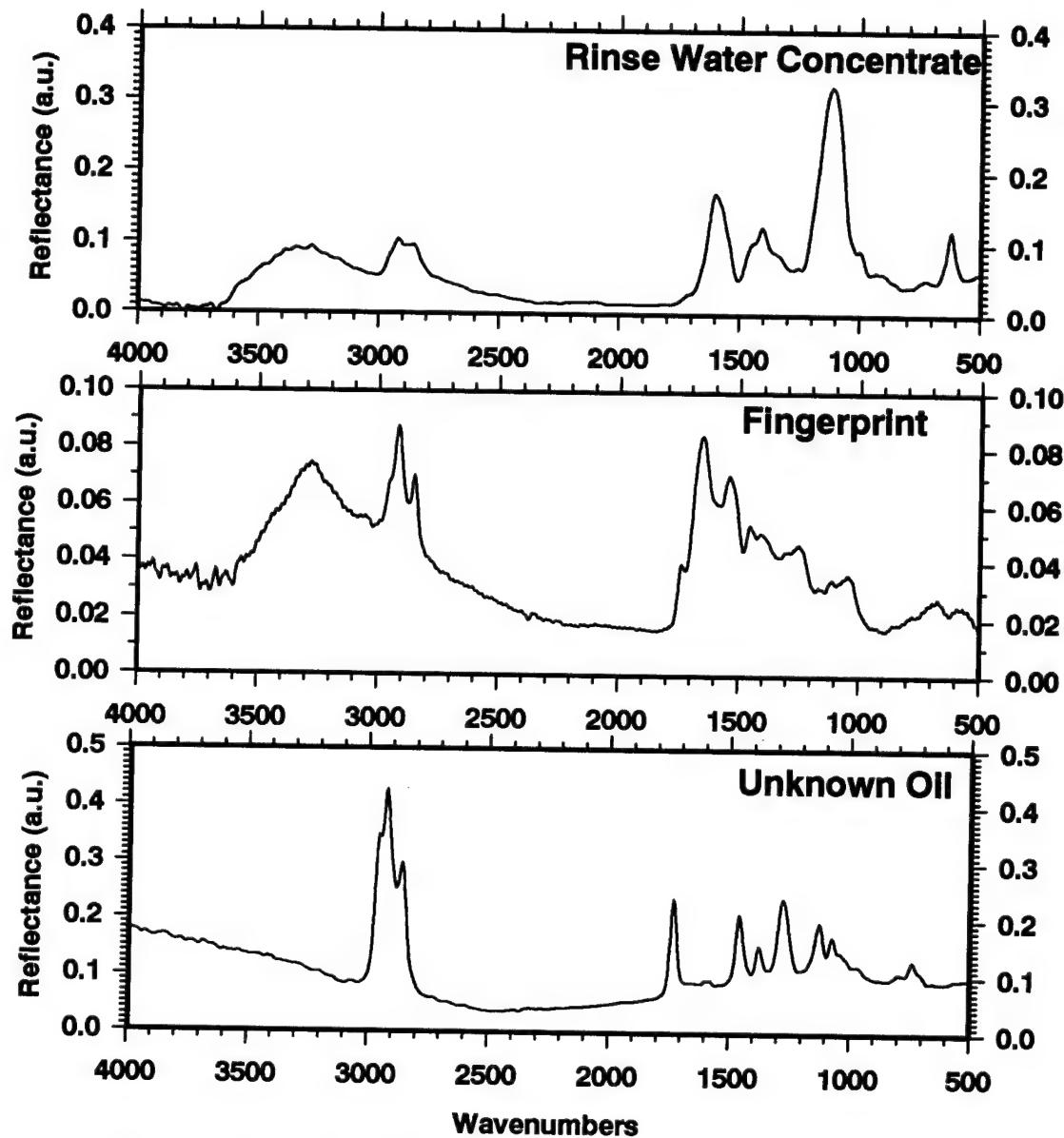


Figure 5. Library spectra obtained using smear applied stains on sandblasted aluminum, demonstrating the unique patterns of surface contaminants suspected to be contributors to contamination on black oxide finished steel gears.

other distinct bands. A search of a large commercially available library would probably identify this oil by its commercial name. The point to be made thus far is that surface inspection depends strongly on knowing what to look for. Library development is a critical part of this inspection process. Libraries should be developed to include the likely contaminants while not overloading the library with unlikely candidates.

3.2 INSPECTION OF BLACK OXIDE STEEL GEAR PARTS

As part of the introduction of the CCAD to the SOC 400 SIMIR, a number of black oxide finished steel gear parts were analyzed. This was in part an exercise in inspecting large objects of peculiar shapes, and in part as an exercise in inspecting surfaces that were neither flat nor sandblasted. Figure 6 shows data obtained from several locations of these parts. Gear teeth were among the easier surfaces to address with the SOC 400. The gear tooth spectrum (Figure 6) appears to represent the infrared absorption spectrum of black oxide finish on a relatively clean steel gear. These are broad bands between 1700 and 1400 cm^{-1} that appeared to vary in relative intensity from part to part and place to place on the same part. This is supported by the fact that spectra from the non-black area (an area where the oxide had been worn off) did not demonstrate these bands. The non-black area did show evidence for an aliphatic ester contaminant. This contaminant was observed on a number of other parts as indicated by two examples obtained from a sun gear spline area. This contaminant was first thought to be the unknown oil shown in Figure 5, but closer examination indicated that all the bands from the unknown oil (Figure 5) could not be found. This exercise did demonstrate that the presence of organic contaminants could be found on ordinary metal parts under conditions where the presence of this contamination could not be detected visually.

CONCLUSIONS

A small, user friendly, light weight, field hardened, computer controlled device for performing surface inspection based on infrared spectroscopic analysis, with high sensitivity of trace contamination on surfaces, is now available for detecting surface contamination, particularly organic contamination on metals. The SOC 400 SIMIR brings to the workplace an inspection capability for detecting trace amounts of contamination on metal surfaces that may otherwise go undetected. The SOC 400 SIMIR is supported by a tremendous existing base in science and technology for use in certifying the cleanliness of metal surfaces at levels that have not been previously available. The job remaining is to develop the practice of the practical inspection of real parts based on a sound knowledge of potential contaminants and their qualitative and quantitative analytical determination.

ACKNOWLEDGMENTS

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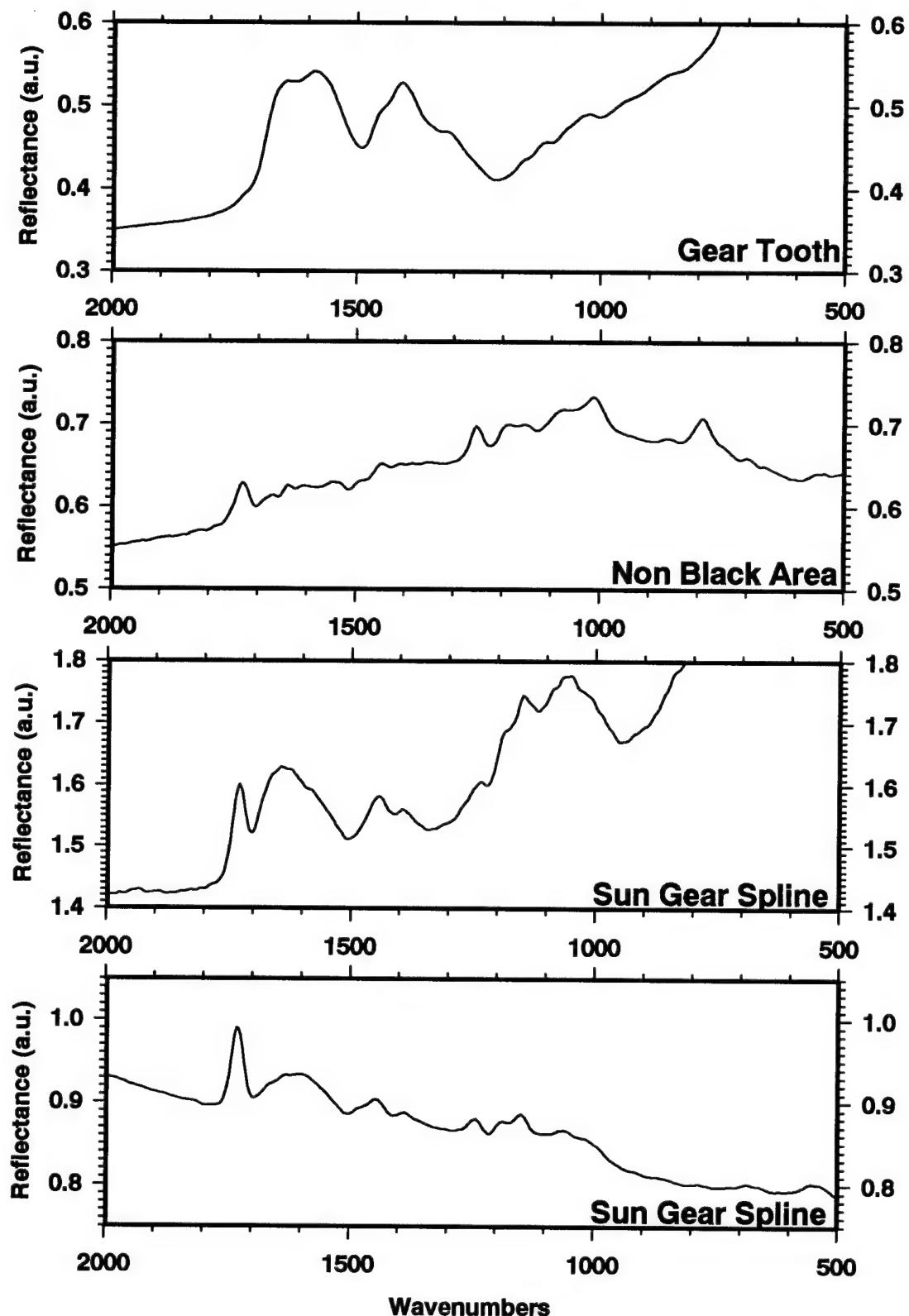


Figure 6. Spectra obtained from black oxide finished steel gear parts. The broad bands appear to be features of the black oxide and their relative intensities. Contamination by an aliphatic ester oil was detected as the 1735 cm^{-1} band.

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LOW COST WET ABRASIVE BLAST PROCESS FOR LEAD PAINT REMOVAL

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ABSTRACT

TRIDENT Refit Facility (TRF) has worked closely with vendors and local regulators to develop a wet abrasive blast paint removal process. This work was initiated when dry abrasive blast operations in their drydock were shut down due to the associated air emission requirements. This action directly affected the command's ability to accomplish its fundamental mission to refit ballistic missile submarines. TRF identified two vendors to help resolve the problem. The first vendor had developed a new system for wet abrasive blast. Introduced in the European market in 1984, the TORBO blast system was brought to the United States in 1992 when it was presented at a national conference of the Steel Structures Painting Council. It is used by Departments of Transportation in many states in the process of preserving bridges. The second vendor had developed an abrasive additive, Blastox, which reacts with the lead paint chips to create a waste product that can be designated as nonhazardous. The wet abrasive blast process developed was first used on the USS MICHIGAN (SSBN 727) hull. It is now routinely used whenever exterior hull paint removal is required. The most important outcome of this process development is that it will permit TRF to pursue work packages involving hull paint removal into the indefinite future.

1. INTRODUCTION

In parallel to the development of the TORBO system at TRF a closed loop, Ultra-High Pressure Water-Jet System (UHP WJS) for depainting large ships was developed as part of the U. S. Navy Advanced Technology Development (ATD) Program. This closed-loop system is capable of removing coatings from underwater hull areas using recycled ultra-high pressure water. The need for the system was initially addressed for the Navy by researchers at the David Taylor Research Center in Bethesda, Maryland. They found that high-pressure cavitating water jets offered the best alternative to abrasive blasting for underwater hull paint removal.¹ Later as higher pressures were implemented, it was found that the high pressure alone was sufficient to erode the paint. The UHP WJ System has proven itself successful in cutting the cost of depainting the hulls of several ships. Following a brief explanation of the two systems, the documented success of the TORBO system on the USS Michigan hull will be addressed. By keeping the system simple and capturing lead in the Blastox, the cost of depainting can be reduced to one fourth of that which was necessary to sand blast the hull of the USS Ohio (SSBN 726) using dry blasting and containment.

2. SYSTEM DESCRIPTIONS

This section explains the TORBO Wet Abrasive Blasting System and the Ultra-High Pressure Water-Jet System. In order to clearly understand the advantages and disadvantages of these systems, the reader must have a good understanding of the systems under comparison.

2.1 TORBO

The TORBO system consists of a pressure vessel assembly with loading hopper assembly, a control cabinet assembly and support components. A unique safety innovation only available with TORBO equipment is the Control Magnet. The Control Magnet is fastened to the wrist of the operator and functions to shut down the system if the operator loses control and the blasting hose begins whipping out of control. This significant improvement in the area of control, coupled with the unique design of the equipment which reduces airborne particulate, makes open air blasting possible again. Two other items of safety equipment that are required in addition to the standard personal protective equipment, are a respirator and protective coveralls, full-face air supplied respirators are required when below the maximum beam line.² These are required because of the high volume of mist containing paint particulate and Blastox. This wet abrasive system is much simpler than the UHP WJS. The simplicity of the design reduces the up front cost and the maintenance requirement. Although it is versatile in the types of abrasives that it can support, this system is restricted to dry docks which have a closed loop drainage system. Because the TORBO system does not have its own water reclamation system, it is restricted to dry docks with such a system.

2.1.1 PRESSURE VESSEL AND LOADING HOPPER ASSEMBLY

The pressure vessel is the primary component of the TORBO system. The loading hopper is used with the installed water pump for loading the abrasive into the pressure vessel. Water and abrasive are washed together through the hopper into the pressure vessel. As indicated, the abrasive does not have to be dry, but can be wet when loaded in the hopper. The vessel has a sealing disc that shuts against water pump pressure. The pressure of the vessel and the flow rate of blast water are controlled at the control panel.

2.1.2 CONTROL PANEL

The control panel consists primarily of gages and valves to regulate the air and water pressures and flow rates. The system is activated at the nozzle when the Control Magnet is placed in the receptacle on the 3-Way Remote Control Switch. The switch is turned off by removal of the Control Magnet from the switch. The three blasting options are Blast Mode, Blowdown Mode and Washdown Mode. Although this system is much simpler than the UHP WJ System, the operators require significantly less training in the proper control settings and blasting methods.

2.1.3 BLAST MEDIA

The TORBO unit may be used to blast with various media. TRF uses copper slag mixed with 20% Blastox. Blastox is a cement-like material containing calcium silicates and calcium aluminates. The TDJ Group, Inc. has patents pending on the proprietary chemistry of this mix that was introduced in 1991 as a chemical stabilizer. The environmental Protection Agency, EPA, and the Naval Sea Systems Command have both approved of Blastox for unrestricted use without hazardous waste treatment permits. It is the standard on which the current Best Demonstrated Available Technology, BDAT, as reported on the EPA RCRA Hotline, is based. Furthermore, a blend of abrasive media with 15% Blastox used at 8 lb./sq. ft. will reduce leachable lead levels from as high as 100 mg/liter to below 5 mg/liter (5 ppm), which is the EPA limit. The blast process is safe and has been proven to consistently stay well below the 0.030 mg/CM³ OSHA action level.

Although adding Blastox to the abrasive media adds at least \$60/ton to the cost, the savings in hazardous waste disposal costs can be as much as 75%. This cost savings is an important factor when added to the environmental benefit of lead encapsulation. Because the wet TORBO - Blastox mix when sprayed against the hull leaves a mist, the mist needs to be washed off the hull at least shifly. Pressure washing the hull adds to the facility's water treatment costs, but ensures that the hull's surface is not adversely affected by the Blastox film.

2.2 ULTRA-HIGH PRESSURE WATER-JET SYSTEM

The closed-loop, Ultra-High Pressure Water-Jet System, UHP WJS, is composed of three major subsystems: a nozzle mounted on a six axis manipulator, a high pressure hydro-pump, and a mobile water recovery subsystem. Ultra-high pressure water from the pump is sprayed onto the hull, with sufficient force to displace the paint. Paint and primer are removed, leaving a near white metal finish. The loose particles of paint and primer are vacuumed into the return line of the mobile recovery unit and processed out as a sludge. The water in that return line is processed for reuse. The goal is to have 100% recovery of the process water and to recirculate that water to the maximum extent possible.

2.2.1 END EFFECTOR SUBSYSTEM

This is the focal point of the total system. It is in this robotically controlled subsystem that the six inch waterjet nozzle is mounted and rotated for transversing a 52 inch by 78 inch area. The waterjets of the nozzle are effective in fully removing, salt, rust, grease, and various paint systems. The nominal pressure of the water at the nozzle is 36,000 psi. Industry standard presently sets 25,000 psi as the lower limit for ultra-high pressure water jetting.

2.2.2 HIGH PRESSURE PUMP SUBSYSTEM

The high pressure pump subsystem consists of dual, intensifiers mounted on a trailer. These Hydro-Pac pumps deliver a non-pulsating flow of water to the supply lines. Experimental research showed that optimum paint removal rates could be achieved by evenly distributing the water energy at the highest achievable pressure. Associated water lines, hoses, valves and fittings were designed to minimize pressure losses. The water supply is provided by the recovery system. The minimum specifications for water pressure and flow rate are 36,000 psi at 10 gpm in order to achieve the desired removal rates. These specifications drove the design requirement to a hydraulic pumping system powered by a 325-horsepower diesel motor.

2.2.3 MOBILE RECOVERY SUBSYSTEM

This subsystem consists of the mobile vacuum recovery unit that recovers the water from the blast head and processes it for reuse. The effluent containment device surrounding the water-jet blast nozzle has a strong vacuum that is capable of containing all of the process water and paint chip residue and preventing it from falling to the dock floor. The mobile recovery unit has various interconnected subsystems, such as the diesel-powered electric generator, air compressor, vacuum unit, liquid/solid separator, water recovery/recirculation system, and deionization system, all mounted within the utility trailer. The liquid/solid separator removes suspended particulate from the effluent stream prior to entering the water reclamation unit. In the reclamation unit the water is processed through a centrifugal separator and several purification filters before it is deionized. The mobile recovery system segregates, filters, purifies, and deionizes prior to return to the nozzle through the high pressure pump. The requirement for the hydro-pump to need minimal water filtration drove the criterion for accepting only water with particles greater than one micron.

3. PERFORMANCE ASSESSMENT

3.1 PAINT REMOVAL

The UHP WJS has been used on several hulls by Puget Sound Naval Shipyard (PSNS). It has been evident that the expected stripping rate and time requirement to set up the end effector in each subzone has not been realized. At 6.5 minutes per subzone, it was hoped that 200 subzones could be depainted in a 10 hour shift. This would amount to 3200 sq. ft. per shift with the 48 inch by 48 inch manipulator frame. With the 52 inch by 78 inch manipulator frame, the most productive shift for the UHP WJS wrought only 951 sq. ft. of depainted surface. The TORBO system had a high paint removal rate when depainting the USS Michigan. The nozzles were capable of blasting 120 to 150 sq. ft. per hour. When six blast nozzles were used in parallel, the TRF paint team could depaint in one hour the same area that it takes one shift to depaint with the UHP WJS.

3.2 COMPARISON OF SURFACE FINISH

Both the UHP WJS and the TORBO unit are capable of cleaning the surface of paint, sulfates and chlorides and should be used with a rust inhibitor. Dry abrasive blasting tends to trap contaminants in the crevices as the blast material impinges on the surface.³ Howlett and Dupuy have also shown some other facts regarding the UHP WJS process that would indicate that an optimum surface would be obtained with the use of garnet injected into the jet stream. For example, water jetting alone will not create or change the surface profile of the blasted area. The visual appearance is not that of the white metal finish left by abrasive blasting. If the area has rough mill scale, the surface may still need to be prepared by hand prior to painting to ensure an adequate surface finish. Since the UHP WJS process does not leave a surface profile as does the abrasive blasting process, it should be used only on materials that have been previously blasted.⁴

3.3 WORK SCHEDULE AND MANNING

The UHP WJS is typically operated for two ten hour shifts per day for six days per week. The minimum work crew consisted of one paint supervisor, two equipment operators, and two maintenance mechanics. The crew was augmented with one additional equipment operator per shift to assist in guiding the blast frame onto the hull and reduce operator fatigue. Painters at TRF, Bangor worked two 12 hour shifts, around the clock for 14 days. To support six blasters in operation, TRF purchased eight TORBO units. Each shift had six painters who stripped the hull with their individual blast nozzles. Additionally, there averaged four support personnel for delivering and filling hoppers with blast media and cleaning up the grit as the stripping progressed. The support personnel were also used for cleaning the TORBOs as the cement-like Blastox solidified in vessel. The team was well coordinated and factory trained in order to support this type of accomplishment in such a short time frame.

3.4 MAINTENANCE AND PERFORMANCE IN THE INDUSTRIAL ENVIRONMENT

Because of the complexity of the UHP WJS, there are many subsystems within systems allowing ample opportunity for equipment malfunction or shutdown for repair or preventive maintenance. The list below documents some of the difficulties with this highly complex system over the past year of evaluation by PSNS:

Fasteners broken/loosen during shipping
Diesel for air compressor failed to start
Conductivity meter pegged high
Micro separator centrifuge required cleaning
Lifting lug crack needed repair

Sheared bolt on intensifier
Dri-prime pump clogged with paint chips
Dead battery on intensifier support diesel
Shaft seal failure on six nozzle drive's motors
Nozzle rotation problem limits travel speed

Centrifuge filled with paint chips	Transporter cable needed repair
Paint chip barrel filled with water	Spurious shutdown of end effector drives
Leak in swivel body shaft seal	Loose bearing on frame tilt mechanism
Intensifier hydraulic cylinder leak	Broken suction piping
Intensifier check valve failures	Make-up water pump did not cycle on to fill tank
Boom failed to extend	Z-axis retraction repair
Proximity switch leak on intensifier	Failed UHP water lines (13 hoses)

System improvements are gradually increasing the removal rate of this developing technology.

The TORBO system is shutdown every 45 to 60 minutes for replenishment of the blast media. The workers would prefer a system that let them blast for at least 150 to 200 minutes before having to refill the vessel. The nozzles used for blasting the USS Michigan experienced some erosion which has occurred after a longer period when blasting with river sand.

3.6 USS MICHIGAN DEPAINTING PROJECT

The first sand blasting ever accomplished in the TRF dry dock was the initial use of the TORBO Wet Abrasive Blasting System to depaint a submarine hull. Although documents vary slightly on the details, Table 1 shows some of the documented results from using six TORBO units to depaint the entire hull of the USS Michigan (SSBN 727).

Area Depainted	65,000 sq. ft.
Time Frame / Schedule	14 days / 2 twelve hour shifts
Deployment	6 of 8 TORBOs stripping
Depainting Rate	120 to 150 sq. ft. / hr
Blast Media Rate	2 to 4 lb. / sq. ft.
Blast Media	Copper slag with 20% Blastox
Water Rate	5 gallons / hr / machine
Inhibitor	1:250 Rust-Lick-B
Depainting	3464 man hours
Media Disposal	96 tons @ \$54/ton = \$5184

Table 1 TORBO Wet Abrasive Blasting System usage on at TRF, Bangor

The combination of more efficient blasting with the TORBO and the chemical stabilization of the lead in the paint chips with the elimination of the requirement for full containment saved TRF 10,000 man hours and nearly \$500,000 dollars.⁵

4. COST COMPARISON

The cost comparison performed in this section was based on Trident submarines. The Trident submarine was chosen since there were recent projects which have accomplished the task of complete depainting and hull preservation as part of the Engineered Overhaul. The approximate hull area to be depainted does affect some of the other factors in the cost comparison. Figures for the dry abrasive blasting of the USS Ohio were obtained from Job Order - Key Op charges and a broader cost comparison being performed in the Industrial Engineering and Planning Division⁶. The data for the TORBO Wet Abrasive Blasting of the USS Michigan is provided by the Trident Refit Facility. In the case of the labor charges, the 4040 man hours to TORBO

blast the USS Michigan were separated into the various categories based on good technical judgment. The total labor charge of 4040 man-hours, however, remains the same. Data from the first two UHP WJS projects, the USS Leftwich and the USS Paul F. Foster, were used to extrapolate and calculate rate and cost data. While the performance data was obtained in fiscal years 1993 through 1995, the cost data for labor rate, utilities, abrasive media, and waste disposal are in fiscal year 1996 rates.

4.1.1 COST COMPARISON DETAIL

Table 2: Dry Abrasive Blasting Vs. UHP WJS and TORBO

	Dry Abrasive	UHP WJS	TORBO
CONTAINMENT			
Manuf/Install/Remove	1500 man-day	N/A	N/A
Labor	\$700,500	\$0	\$0
Fabric Cost	\$17,500	\$0	\$0
Containment Total	\$717,500	\$0	\$0
PAINT REMOVAL			
Labor in Open Areas			
Removal Rate per Nozzle	261 sq. ft./hr	204 sq. ft./hr	140 sq. ft./hr
Number of Nozzles	6	2	6
Percent Time Stripping	14.5%	20.0%	27%
Number of Blasters	6	4	6
Number of Support People	3	2	6
Dry Abrasive Blast Labor	25 sq. ft./man-hr	N/A	N/A
Labor Near Protrusions			
Removal Rate per Nozzle	N/A	40 sq. ft./hr	N/A
Number of Nozzles	N/A	6	N/A
Percent Time Stripping	N/A	10.0%	N/A
Number of Blasters	N/A	6	N/A
Number of Support People	N/A	2	N/A
Man-Days for Paint Removal	324	916	360
Depaint Labor Total	\$151,300	\$427,800	\$168,120
Blast Material			
Abrasive Usage Rate	12.5 lb./sq. ft.	N/A	2.6 lb./sq. ft.
Abrasive Usage	406 tons	N/A	84 tons
New Abrasive Cost	\$70/ton	N/A	\$205/ton
Total Abrasive Cost	\$28,500	N/A	\$17,220
Number of Manlifts Required	N/A	N/A	6 for 2 weeks
Manlift Rental Cost	N/A	N/A	\$1200/week
Total Manlift Rental Cost	N/A	N/A	\$14,400
Blast Material Total	\$28,500	N/A	\$31,620

Utilities

Compressed Air Required/Nozzle	250 cfm	N/A	190 cfm
Total Hours of Nozzle Time	249 hrs	N/A	454 hrs
Total Compressed Air Cost	\$4,100	N/A	\$5700
# of Dust Collectors	2	N/A	N/A
Dust Collector Motor Size	75 hp	N/A	N/A
Dust Collector "On" Time	289 hrs	N/A	N/A
Total Electricity Cost	\$1,370	N/A	N/A
Diesel Fuel/Blast Hour	N/A	25.56 gal/hr	1.5 gal/hr/manlift
Total Diesel Fuel Cost	N/A	\$6,210	\$470
Utilities Total	\$5,470	\$6,210	\$6,170

Maintenance

Maintenance Ratio	0.30	0.20	0.07
Total Maintenance Man-hours	74.7 hrs	70.4 hrs	32 hrs
Maintenance Materials	\$0.05/sq. ft.	\$0.50/sq. ft.	\$0.05/sq. ft.
Total Maintenance Materials	\$3,250	\$32,500	\$3,250
Maintenance Total	\$7,610	\$36,610	\$5,120

Waste Disposal

Abrasive Clean-up

Bulk Abrasive Removal MH	700 hrs	0	264 hrs
Clean-up Total	\$40,860	\$0	\$15,411

Blast Debris

Abrasive Disposal Cost	\$390/ton	N/A	\$54/ton
Paint Chip Disposal Cost	N/A	\$2.08/lb.	N/A
Paint Chip Weight	0.375 lb./sq. ft.	0.375 lb./sq. ft.	0.375 lb./sq. ft.
Amount of Waste Generated	418.4 tons	12.2 tons	96 tons
Blast Debris Waste Total	\$163,200	\$50,700	\$5184

Waste Water

Water Usage Rate	N/A	N/A	5 gal/hr
Actual Washing Time	N/A	N/A	288 hr
Hull Rinse Water	N/A	N/A	2800 gal
Total Water Used	N/A	N/A	5120 gal
Dry Dock Rinse Waste Tot	\$0	\$0	\$770

TOTAL PROJECT COST	\$1,114,450	\$521,320	\$232,400
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PERSPECTIVES

Approximate Duration	17 days	39 days	14 days
Containment Cost	\$11.04/ sq. ft.	\$0	\$0
Blast Rate	226 sq. ft./man-day	71 sq. ft./man-day	191 ft ² /man-day
Blast Material Cost/ sq. ft.	\$0.44/ sq. ft.	\$0	\$0.49/ sq. ft.
Disposal Cost/ sq. ft.	\$3.14/ sq. ft.	\$0.78/ sq. ft.	\$0.21/ sq. ft.
Project Cost/ sq. ft.	\$17.15/ sq. ft.	\$8.02/ sq. ft.	\$3.35/ sq. ft.
Area Blasted =	65,000 sq. ft.		
Labor Rate =	\$467/man-day		
Water Processing Cost =	\$0.15/gal		
Percent "Open" Area =	85%		
Compressed Air =	\$0.0011/cf.		
Cost of Electricity =	\$0.0423/kw-hr		
Cost of Diesel Fuel =	\$0.69/ga		

4.1.2 COMMENTS ON COST COMPARISON DATA

The containment labor was the actual charged labor and the fabric cost was calculated based on current fabric prices. It was assumed that the staging that supports the containment is part of the ready inventory normally available at a naval repair facility, so the cost of the staging was not included. No containments are necessary for the UHP WJ System because of its design for complete water recovery. Because of the ability of the Blastox to encapsulate the lead when TORBO blasting, no containment is necessary in this case either. If the project needed to do concurrent work in the dry dock, that containment would be an additional cost. If an inert abrasive were not readily available, some dry docks could require partial containment to prevent the abrasive from entering the dry dock drains. This cost was not taken into account since the TRF has a water treatment facility and the PSNS dry docks are being retrofitted with special drain piping that will also allow water recovery. Also included was the installation of temporary facilities such as lighting and breathing air associated with dry abrasive blasting in containments. It was also assumed that these temporary facilities were available at the shipyard and were not purchased for this project.

On this project it was assumed that for the use of the UHP WJS that 85% of the areas were assessable with the manipulator frame. The inaccessible areas are depainted with three smaller hand held nozzles that can be connected to the water reclamation system. The data for the hand-held attachments is estimated, since there has been limited use of these accessories to date. The open area removal rate is based on a 1.5 inch per second automated travel speed. The percent stripping time for the UHP WJS is unfortunately much lower than was anticipated by the designers and the operators, but reflects what has been achievable to date.

For the dry abrasive blasting and the TORBO blasting, the percent stripping time reflects that which has been achieved. In these cases the lower rate has more to do with personnel endurance than material condition.

The dry blast grit was copper slag. The abrasive used by the TORBO system was copper slag with 20% Blastox. Other abrasives may have a greater or lesser removal efficiency, but would provide similar results for comparison. Note that the manlifts used to reach the hull are considered a material cost in this section. These were needed only by the TORBO blasters. Although manlifts are usually available with advanced notice in most shipyards, the cost was included here since the UHP WJS is purchased with the transporter.

The utility figures were based on Public Works Center information provided in the cost analysis for PSNS⁷. The UHP WJS is self powered by its own generator and compressor, hence diesel fuel is the only utility.

While the maintenance ratio is estimated for the dry blast and wet blast cases, the actual data for the UHP WJS is used. The notional maintenance ratio was used to extrapolate the costs from small depainting projects to the larger Trident depainting project. The unproductive man-hours that accumulate during maintenance periods is included in the labor figures since it effects the percent stripping time. Since a maintenance man already supports the UHP WJS, the maintenance ratio is lower than if compared equally to the other methods.

Waste handling and disposal vary significantly among the three processes. If the project was removing only lead free paint, the disposal costs would be drastically different. The dry grit disposal cost would be reduced to \$22,600 from \$163,200. If the paint chip residue in the 55 gallon drums of the UHP WJS were considered industrial waste, the disposal cost would be much less. Instead of costing \$2.08/lb., the disposal cost would be about \$1.49/lb. The nationwide disposal costs vary greatly based on location and availability of landfills.

The actual duration of the projects varied based on the resource support that the depainting team received from the rest of the project. The team required to erect the containment for dry blasting needs is larger when the time in the dock is shorter. The 17 day duration is shorter than that accomplished on the USS Ohio because there were other factors involved. For this comparison, it was assumed that 30 men per shift from various trades were available for building the containment. The containment installation team would begin three days prior to the depainting and continue through the depainting process until two days after the depainting was complete. The sand blasting process would last 12 days, if continued for three shifts per day with the nine man team. For the UHP WJS, the 39 day duration was based on the stripping rates using two systems with either two or six nozzles depending on proximity to protrusions. The 14 day duration was actually accomplished at the TRF by the USS Michigan depainting team using the TORBO system.

5. CONCLUSIONS

The cost comparison above does not include the capital outlay for basic abrasive blast equipment. The UHP WJ system is approximately \$1,300,000 per unit. The analysis above is based on depainting rates requiring the use of two units. Eight sets of TORBO equipment were purchased by TRF for approximately \$250,000 total. The cost of the UHP WJ system is expected to decrease with expanded use. TRF is already scheduled to depaint six more Trident submarine hulls. It is clear that use of the TORBO system will provide savings of approximately \$4,000,000 while protecting the environment.

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TECHNICAL SUPPORT FOR IMPLEMENTATION OF ALUMINUM ION VAPOR DEPOSITION TECHNOLOGY

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ABSTRACT

Industrial production and maintenance activities conducted at Army depots typically include metal plating operations. For many years, cadmium has been commonly applied as a surface coating, using conventional electroplating processes, to provide a protective, corrosion-resistant finish. Cadmium is a toxic, carcinogenic metal and cadmium electroplating generates sludges, rinse waters, and spent plating solutions. Alternatives to cadmium electroplating exist. In many cases, aluminum coatings can be substituted for cadmium coating to provide corrosion protection and other functional requirements. Aluminum ion vapor deposition (AIVD) is a process that can be used to plate aluminum on metal parts. This technology, which was originally developed in the 1970's for use on aircraft parts, does not generate the rinse waters, sludges, or spent electrolyte solutions that are associated with conventional electroplating. With the exception of a small quantity of waste generated during periodic cleaning of internal components of the system, AIVD coating generates no wastes.

The U.S. Army Environmental Center (USAEC) provided technical assistance to Tobyhanna Army Depot (TOAD) in regard to acquisition of an AIVD system. Information acquisition efforts included completion of site visits to facilities using AIVD to discuss and observe the operation and use of this technology in depot operations. Site visits to TOAD were also conducted to discuss and review current cadmium plating operations. Outputs of this technical support effort included Trip Reports, a Bid Specification for an AIVD system, an Economic Analysis (EA) for an AIVD system, a Work Order for installation of an AIVD system, and the collection of information on AIVD technology and coatings. This paper reviews the technology and its applicability at Army depots including discussion of costs, waste reduction, and other benefits (such as reduction of employee exposures to toxic metals).

1.0 INTRODUCTION

The Environmental Technology Division (ETD) of the USAEC conducts research and development to support environmental compliance at Army depots, ammunition plants, arsenals, and other Army installations and activities where industrial manufacturing and maintenance is conducted. Since the outset of the U.S. Army's hazardous waste minimization (HAZMIN) program, the USAEC has been an active supporter of HAZMIN initiatives at all Army industrial operations. Previous initiatives relating to U.S. Army Industrial Operations Command (IOC) facilities have included the demonstration and implementation of AIVD at Anniston Army Depot (ANAD).¹ Subsequent to the successful application of AIVD at ANAD, Corpus Christi Army Depot (CCAD) also implemented the use of AIVD technology. Most recently, the USAEC provided support for technology transfer and implementation of AIVD at TOAD.

1.1 BACKGROUND

Industrial production and maintenance activities conducted at Army depots typically include metal plating operations. For many years, cadmium has been commonly applied as a surface coating, using conventional electroplating processes, to provide a protective, corrosion-resistant finish. Cadmium plating offers good corrosion resistance in salt-water environments, provides a good base for soldering, and has a low coefficient of friction that gives cadmium-plated fasteners good threaded connections with low applied torque.¹ However, cadmium is a toxic, carcinogenic metal and cadmium electroplating generates sludges, rinse waters, and spent plating solutions. These residuals contain cadmium and are listed hazardous wastes under the Resource Conservation and Recovery Act (RCRA). Treatment of the rinse water and spent solutions also generates RCRA hazardous waste and that require special handling and disposal.

Alternatives to cadmium electroplating exist. In many cases, aluminum coatings can be substituted for cadmium coating to provide corrosion protection and other functional requirements. Aluminum can be applied by metal spraying, cladding, electroplating, or ion plating.² AIVD is a process that can be used to plate aluminum on metal parts. This technology does not generate the rinse waters, sludges, or spent electrolyte solutions that are associated with conventional electroplating. With the exception of a small quantity of waste generated during periodic cleaning of internal components of the system, AIVD coating generates no wastes.

At ANAD and CCAD, AIVD coatings have been successfully substituted for cadmium electroplated coatings on a variety of metal parts. Substitution of AIVD coatings for cadmium electroplated coatings can significantly reduce the volume of RCRA hazardous wastes that are generated by depot operations. It also reduces employee exposures to cadmium and other toxic components (e.g. cyanide and corrosive solutions) that are used in the conventional electroplating process.

Multiple regulatory incentives for substitution of cadmium coatings exist and are summarized in the draft "Strategic Plan for Eliminating Cadmium from United States Army Tactical Weapon Systems" prepared by the Army Acquisition Pollution Prevention Support Office.³ Regulation of cadmium usage and contamination has become increasingly more restrictive. This trend is expected to continue in the future. Increasing costs and increasing impediments to plating operations are associated with more stringent regulation. Implementation of alternatives to cadmium electroplating is being actively pursued by the Army to minimize the generation of hazardous waste and to ensure protection of worker's health and the environment.

1.2 SCOPE AND OBJECTIVES

The scope of the work documented herein was focused on providing technical assistance to TOAD in regard to acquisition of an AIVD system. Outputs of this technical support effort included a Bid Specification, an Economic Analysis (EA), and a Work Order for acquisition of an AIVD system at TOAD, and the collection of information on AIVD technology and coatings.

2.0 CADMIUM AND ALUMINUM COATINGS

2.1 ELECTROPLATED CADMIUM COATINGS

Cadmium is a soft, ductile, silver-white metal.⁴ Electroplating of elemental cadmium onto the surface of metal (e.g., fabricated steel and cast iron) parts has been commonly practiced by the military for over 50 years. Cadmium coatings offer excellent corrosion resistance in salt water environments and extend the life of metal components, such as those constructed of high strength steels. In addition to corrosion resistance, cadmium's natural lubricity enhances its use on threaded fasteners. It is also readily solderable and serves as a good substrate for finish coatings (i.e., chromate conversion coatings and paint finishes). Ease of electroplating and high rates of deposition in addition to the desirable characteristics of the coating resulted in the widespread use of this surface plating technology.⁴ Electroplated cadmium coatings have been used on components of military equipment for many years and numerous military specifications for metal parts

require the use of cadmium coatings. Requirements for electrodeposited cadmium coatings are specified in MIL SPEC QQ-P-416E, February 1987.⁵

Cadmium electroplating is typically carried out in an aqueous bath of cadmium oxide and sodium cyanide and other electrolytes.⁶ The part being plated serves as the cathode in the electrolytic cell and the cadmium solution serves as the electrolyte. Plating operations at Army depots typically involve relatively large (e.g., 4 ft wide by 10 ft long by 4 ft deep) open top plating tanks. Push-pull ventilation systems are typically used to control fumes. At TOAD, the typical sequence of cadmium plating operations is: ultrasonic cleaning, caustic dip, hydrochloric acid dip (to strip old cadmium coatings), cadmium electroplating, chromate conversion coating, and finish painting.⁷ Water rinses are conducted between operations.

Cadmium is a toxic metal and proper handling of the metal and industrial residues is required. Acute industrial poisoning can occur through the respiration of cadmium dusts or fumes during common operations such as melting, welding, or heating of cadmium-plated steel.⁴ Regulation of cadmium in the workplace and in the environment has continued to become increasingly more stringent. The Occupational Health and Safety Administration (OSHA) regulations set the permissible exposure limit (PEL) for cadmium at 5 $\mu\text{g}/\text{m}^3$ in workplace breathing air.³

Cadmium can contaminate the workplace at Army depots through a variety of sources related to cadmium electroplated surfaces. Cadmium solutions and fumes must be managed during the electroplating operation. Dragout of cadmium on plated parts contaminates rinse waters which require subsequent treatment prior to discharge. The sludges generated at the wastewater treatment plant also become contaminated with cadmium. Additionally, during repair and maintenance activities, cadmium plated parts are routinely handled. Stripping of surface coatings, including cadmium electroplates, is accomplished by both physical and chemical means. These operations generate cadmium contaminated residuals such as spent shot blast media and chemical stripping solutions and sludges. Management and disposal of cadmium containing wastes and residuals is regulated under the hazardous waste regulations of the RCRA and under the Clean Water Act (CWA) by the U. S. Environmental Protection Agency (USEPA).

Increasingly more stringent requirements stipulated by environmental and health protection regulations have resulted in increasing costs associated with cadmium electroplating. Both the current costs associated with meeting requirements, such as waste management, transport and disposal, medical monitoring, record keeping, preparation of manifests, and the potential future costs that may be associated with potential future liabilities resulting from disposal of hazardous wastes, have impacted the use of this process. It is anticipated that tighter regulatory restrictions and increasing costs associated with meeting these environmental and health related restrictions will continue for the foreseeable future.

Methods to minimize the wastes generated and engineering controls to enhance workplace safety must continue to be employed and expanded. Generation of wastes (sludges, liquids, and gaseous emissions) is inherent to cadmium electroplating operations. The most effective control of cadmium contamination is process substitution and elimination of most or all of the cadmium electroplating conducted at Army depots.

2.2 AIVD COATINGS

Aluminum is a soft, light, odorless, tasteless, nontoxic, nonmagnetic, and highly conductive metal.⁴ The formation of a thin, tightly adherent, oxide film provides excellent corrosion resistance.⁴ Aluminum coatings can be applied by metal spraying, cladding, electroplating, and ion deposition.² The ion deposition process is advantageous because of the control of thickness that it affords. Additionally, ion plated coatings typically have good adhesion and are applied at low substrate temperatures (90-150° F).² "Throwing power," the ability of the process to coat complex shaped parts, is another strong point of ion vapor deposition.² The main benefits of aluminum coatings as a substitute for cadmium are that they can provide better corrosion protection while avoiding both worker exposure to toxic metals and the generation of hazardous wastes.⁸ Advances in vacuum coating technology has significantly increased its competitiveness with conventional electroplating.⁹

AIVD technology was developed by the McDonnel-Douglas Aircraft Company to apply a uniform, dense and highly adherent coating of aluminum to aircraft parts.² Since its development, AIVD systems have been installed and operated at over 70 facilities, including both government/military and commercial applications.¹

The Navy uses this technology at both Jacksonville and Pensacola Naval Air Stations. The Air Force confirmed that substitution of AIVD coatings met or surpassed all requirements during testing of parts from multiple Air Logistics Centers by the McDonnell Aircraft Company.⁹ Air Logistics Centers, including Warner Robins, Ogden, Oklahoma City, and Sacramento, operate AIVD systems for coating of aircraft parts and are converting their cadmium plating workload to AIVD coatings. It is anticipated that about 80 percent of the cadmium work load can be converted.⁸ Parts that are too large, or that have deep recesses, are not candidates for AIVD coating and remain part of the workload for cadmium plating lines at these ALC's.

AIVD coatings are also applied during production, as opposed to overhaul and maintenance operations. For example, AIVD is the prime coating used on components of the Patriot, Amraam, and Lantirn projects.¹⁰ Other specialized applications of AIVD coatings include coating of ferrite assemblies on the Patriots phased array radar system.¹⁰ The conductivity of aluminum allows it to be used for electrical bonding and for EMI and RFI shielding.¹⁰ Most recently, AIVD has been used to coat plastics and composites.⁶

Military Specification MIL-C-83488C establishes the requirements for coating low alloy steel, stainless steel, aluminum alloy and titanium alloy parts with high purity (99 percent plus) aluminum.¹¹ For coatings of the same thickness, aluminum provides significantly greater corrosion resistance than cadmium based on the specified salt spray test requirements. For example, a 0.5 mil coating of cadmium must provide 96 hours of resistance (determined by formation of white corrosion products or corrosion of base metal) without a chromate conversion coating and 168 hours with a conversion coating.⁵ The same thickness of aluminum must provide 336 hours of protection without conversion coating and 504 hours with the chromate coating (without evidence of base metal corrosion).¹¹

AIVD generally produces a consistent coating thickness.² Variations in the thickness of the coating associated with the relative position of the parts in the chamber can occur during a single plating run.¹² However, the consistency and thickness of the coating in deep recesses or the interior of holes is difficult to control.¹⁰ Aluminum coatings will be applied in recesses or bores to a depth approximately equal to the diameter. However, the coating typically loses uniformity and thickness at a depth exceeding 0.5 diameter.¹⁰ The AIVD coating, as deposited, has significant microporosity that is a result of the way in which aluminum accumulates on the surface during plating. The AIVD coatings must be densified by peening (burnishing) with glass beads to consolidate the coating.¹² Porous coatings breakdown more quickly, provide less protection from corrosion, and potentially can cause hydrogen embrittlement of high strength steel substrates.¹³

A higher torque is usually required to install an AIVD coated fastener than a cadmium coated fastener because of aluminum's higher coefficient of friction.² Torque-tension relationships have been a concern of the aerospace industry for flight-critical fasteners. As a result of this concern, AIVD coatings have been subjected to rigorous testing and evaluation. The use of a cetyl alcohol lubricant can reduce torque requirements by up to 70 percent.^{2,9} In addition, this concern led to the development of aluminum-teflon paints.² AIVD coated fasteners have been used in aerospace applications for nearly 15 years. Very few reports of problems related to the torque-tension issue have been reported.² In general, it has been found that the use of a lubricant has been adequate and that the differences have not been sufficient enough to warrant changes in installation procedures, tools, or hole sizes.²

While AIVD processing is a technologically advanced system, the degree of operator competence required is similar to that of conventional cadmium electroplating. It has been found by ANAD and CCAD, that the systems are well received by plating shop personnel and that existing personnel could be readily trained and become productive and efficient AIVD operators.

3.0 AIVD PROCESSING

3.1 EQUIPMENT AND OPERATION

Currently, two equipment vendors provide AIVD systems that are similar in function and appearance. Major components of the system include the vacuum chamber, vacuum pumps (a roughing pump, a mechanical pump, and a diffusion pump), parts handling equipment (e.g., dollies, racks, barrel coaters, etc.), and a computer controller. Although the system can be operated manually, computer controllers facilitate use and increase production efficiency. The production area should be clean and air conditioned as the presence of contamination and humidity greatly increase pump down times and can affect the quality of the coating. A separate, positive pressure room which the AIVD chamber opens into, is typically constructed to house the parts handling and operator control area. The size of the work area can be varied, however, sufficient room to allow the use of multiple parts racks and dollies increases productivity.

AIVD is conducted in a cylindrical shaped vacuum chamber constructed of mild steel. The internal size of a standard chamber is approximately 6 ft in diameter by 12 ft long. This yields a usable plating zone of approximately 5 by 10 feet.² System utilities include electricity (e.g., 480 V, 3 Phase, 60 Hz, 300 amp service), argon gas (compressed cylinder supply), non-contact cooling water (~25 gpm at 40 psig) and gaseous nitrogen for the cryogenic pump, and compressed air (60 - 80 psig) to operate vent valves and air ride dollies. Ancillary equipment, such as glass bead peening booths and grit blast booths require compressed air (e.g., 70 cfm at 80 psig) and electricity (460 V, 3 phase, 60 Hz, 3 amps and 110 V, 1 phase, 60 Hz, 6 amps).

Surface contamination, including rust, mill scale, and residues of cleaning, can affect the quality of the AIVD coating including reduced adhesion and less corrosion protection.¹² Subsequent to cleaning, the parts are dry blasted with aluminum oxide (150 - 220 mesh) to prepare the surface for plating.⁹ Cleaned parts to be plated are hung from a rack which is then slid into place in the chamber. Because the surface of the parts must be clean and free of surface contamination, operators typically wear cotton gloves to avoid transfer of skin oils to the parts. The number of parts plated during a cycle and their relative positions and orientation, can affect plating thickness and quality. To facilitate parts loading, specialized dollies that have air flotation pads on the legs allow the parts racks to be easily moved. In addition to standard parts racks and dollies, specialized racks (e.g., rotating racks) and barrel coaters are available. The use of air ride dollies necessitates that the shop area have a flat, smooth floor.

A mechanical pumping system is used to achieve the 9×10^{-6} torr operating vacuum.¹⁰ To decrease pump down times, a cryogenic cooler can be used to remove water vapor present in the chamber. Pump down time is adversely and significantly impacted by the presence of humidity in the chamber. Therefore, the front end of the chamber is located in an air conditioned room. This allows control of humidity and helps to minimize contamination of the parts prior to coating. The only discharge from the system is the exhaust from the vacuum pumps. A single 4 inch diameter PVC vent pipe is used for this purpose. This is the sole discharge from the system. Environmental permits are not required for installation and operation.

Once parts have been loaded into the chamber and the vacuum (10-6 torr) achieved, argon gas is introduced to raise the pressure to about 6×10^{-3} torr. A high-voltage negative potential is applied to the substrate which generates a plasma within the chamber. The bombardment of the surface by argon ions provides a final cleaning of the parts.¹⁰

Aluminum wire is fed to ceramic boats that are electrically heated to 2000° F. The aluminum vaporizes and is deposited on the surface of the parts hung in the chamber. The boats are mounted on a motorized, movable rack which traverses the length of the chamber and back. The number of passes made by the boat rack, the speed of the ceramic boats, and the feed rate of the aluminum wire are critical operating parameters that affect coating thickness, consistency, and quality. While AIVD plating is not a strict line-of-site process, the distance between parts and between the parts and the boats and their relative orientation can affect the thickness and consistency of the coating. Therefore placement of parts is also a critical parameter that must be controlled by the operator. Depending upon the complexity of its shape, the parts may have to be turned and the plating process repeated to ensure complete coverage. Alternately, rotating racks may be

used to move the parts during plating. Depending upon the operating parameters and the level of humidity in the chamber, pump down and plating can take 1 to 2 hours.

At the completion of the plating process, a cool down period of about ten minutes is allowed to elapse. The chamber is then vented to return to atmospheric pressure. The parts rack is then removed from the chamber. At this point, the AIVD coating is porous due to the columnar structure associated with the plated aluminum.⁹ This porosity is reduced and the coating densified by peening (burnishing) the surface with glass beads at 20 - 30 psi in a glove box or blast booth.¹⁰ The peening not only serves this function but also ensures that proper adhesion of the coating to the substrate was achieved.

3.2 WASTE GENERATION

Removable stainless steel liners (thin panels) are used to avoid coating of internal components of the chamber with aluminum. The liners must be periodically removed and cleaned, either by mechanical or chemical stripping, to remove accumulations of aluminum. The panels not only protect the chamber but they also serve to reduce the time required to pump down to vacuum. If the accumulations of aluminum are not removed periodically, their porous nature will trap gases and moisture which will then off gas during pump down. This can significantly increase the time required to achieve the working vacuum. The panels can be stripped chemically, for example by dipping in a sodium hydroxide solution, which generates a caustic residue. This residue is a RCRA characteristic hazardous waste (corrosive) and is the only waste stream directly associated with the AIVD process. Because the depots typically have a sodium hydroxide dip tank as part of their conventional plating operations, this residue is not a new or additional waste. Alternately, the aluminum removed from the shields potentially can be recovered and recycled, though not directly back to the AIVD process.¹⁴ The frequency of cleaning is dependent on production rates and is indicated by noticeable increases in pump down times. The volume of this waste stream is dependent upon the workload put through the AIVD system.

Other wastes are generated during pre- and post-treatment of parts plated by AIVD. However, these treatments are not unique to the AIVD process and are the same treatments commonly used in conventional cadmium electroplating (e.g., degreasing, stripping of existing paint and surface coatings, grit blasting, chromate conversion coating, and finish painting). While such waste streams are not avoided through the substitution of AIVD for cadmium electroplates, they would not become contaminated with cadmium in the case of complete substitution. However, even after implementation of AIVD coating, the pre-treatment of parts during overhaul and maintenance will continue to generate cadmium contaminated residues until all cadmium parts are returned from the field, cycled through the maintenance system, and plated with AIVD coatings.

3.3 COST

The cost of an AIVD system is dependent upon a number of variables including system options, delivery distance, and other factors. Site preparation costs typically will include construction of an air conditioned clean room with a smooth, flat floor that can accommodate the weight of the system and production parts. The estimated cost range for an AIVD system is presented in Table 1. The delivery time for an AIVD system can be anticipated to be in the range of 24 to 36 weeks.

Depending on the application, the capital and operating costs for an AIVD system can be higher than those for conventional cadmium plating.⁶ However, the benefits to the life-cycle costs achieved by the avoidance of hazardous waste generation, worker exposure to toxic metals and corrosive solutions, and the need for ventilation and fume control, can offset this differential. The cost differential is anticipated to continue to decrease in the future as cadmium plating becomes increasingly more expensive due to increasingly stringent environmental and health regulations. Advances in vacuum plating technology which increase productivity and reduce cost are also likely to continue as the use of this technology expands.

TABLE 1. ESTIMATED COST RANGE FOR AN AIVD SYSTEM.

Item	Estimated range, \$
AIVD System (6 by 12 ft chamber)	\$480,000 - \$510,000
Parts racks/dollies (2)	\$44,000 - \$46,000
Barrel coating rack	\$40,000 - \$42,000
Cryogenic pump	\$32,000 - \$40,000
Shipping, installation, training, and spare parts	\$20,000 - \$70,000
Pressure glove boxes	\$15,000 - \$25,000
<u>Site preparation</u>	\$50,000 - \$50,000
Total	\$681,000 - \$783,000

4.0 AIVD PLATING OPERATIONS AT ARMY DEPOTS

During the course of the technical assistance provided under this project, site visits and meetings were held at ANAD, CCAD, and TOAD. The purpose of this activity was to obtain information on the success of implementation of AIVD technology at ANAD and CCAD and to obtain information on lessons learned that could benefit implementation at TOAD.

4.1 ANAD

An AIVD plating system was first installed at ANAD in early 1991 under a previous USAEC demonstration project.¹ Subsequently, a second system has been installed to increase production capabilities. Both systems are co-located in a common shop area. Aluminum coatings are applied to various vehicle and engine parts.

Although the original unit did not include a cryogenic cooler, it has since been retrofitted with one. The bid specification used for the acquisition of the second AIVD unit required a cryogenic cooler. This system component reduces pump down time to approximately 30 minutes and is seen as a critical element for efficient operation. Standard air flotation dollies supplied by the manufacturer are used to hold and move the large parts racks. Multiple dollies and racks were purchased to enhance productivity. The use of multiple dollies and racks allows the operators to load and/or unload parts during AIVD plating cycles. The size of the shop must take into account the number of dollies and parts racks that will be used and must allow room to maneuver them to and from the chamber.

The plating process at ANAD includes pretreatment consisting of vapor degreasing, chemical stripping of existing cadmium or aluminum coatings and, abrasive blasting with aluminum oxide. The blast booths (glove boxes) used for the abrasive aluminum oxide blasting are dedicated for use on parts that will be plated by AIVD (i.e., pretreatment of parts is segregated to avoid contamination of parts with residuals that could affect the AIVD coatings). Subsequent to completion of the AIVD coating cycle, aluminum coated parts are peened (burnished at 20 - 30 psi) with glass beads in dedicated blast booths (glove boxes). The parts then receive a conventional chromate conversion coating.

Depot personnel have modified the parts racks, through the addition of fixed eye bolts and alligator clips, to facilitate the placement and removal of parts. Additionally, operators initiated treatment of the protective shields with boron nitride.¹ This treatment serves as a release agent making removal of aluminum accumulations much easier. Lessons learned at ANAD indicate that both a cryogenic cooler and a computer controller should be included in the equipment bid specifications for any new AIVD system. Additionally, operator training, multiple parts racks and dollies should also be incorporated to maximize the efficiency of startup and operation. Finally, dedication of pre- and post-treatment equipment (e.g., blast booths/glove boxes) was recommended to help minimize contamination of parts which can result in inadequate coatings.

4.2 CCAD

An AIVD system was installed at CCAD in early 1993 and has been successfully used in plating operations since that time. The CCAD is equipped with an automated computer controller (Intel 486 based). This controller is programmed to control all operational parameters including pump down, argon cleaning, the number of passes and the speed of the ceramic boats, and the aluminum wire feed rate. The controller has also been programmed to permit initiation of an automatic startup sequence which initiates warmup of the system prior to start of the production shift. This significantly reduces the initial startup time for the operators. Additionally, the operating parameters associated with specific parts, including the number of parts and their specific placement on the parts racks, can be entered into the system's data base. This historical information assists the operator in ensuring that consistent coatings are applied.

Standard air floatation dollies are used at CCAD. As at ANAD, CCAD operators have made modifications to the parts racks that facilitate parts handling. The addition of eye bolts, fixed in strategic locations on the rack, speed the loading and unloading operations for commonly plated parts. This modification also helps avoid electrical short circuiting that can occur if parts touch or are not properly attached to the rack. The parts racks have been modified by CCAD operators, with the addition of fixed eye bolts, to aid in the placement of parts.

Lessons learned at CCAD confirm that a cryogenic cooler and a computer controller (including a color monitor and 24-pin narrow carriage printer) should be included on any new system. Operator training by the equipment vendor should be included in the purchase package. CCAD operators recommend that a week of initial training be completed prior to actual use. After a month of operating experience is gained, a second week of training is recommended to enhance operator skills and to address problems encountered during initial operations.

A substantial volume of cooling water is currently used by CCAD to operate the system. CCAD operators recommend that the use of a water chiller be investigated as a potential means to reduce the quantity of water required. This would also permit the use of conditioned water that would prevent buildup of calcium scale in the cooling system. Other recommendations included construction of a clean-room large enough to allow use of multiple parts racks and dollies, and inclusion of a pre-award survey at the vendors facility to ensure that the specific equipment to be installed is fully operational prior to shipment. The latter recommendation should help minimize startup times.

4.3 TOAD

TOAD supplies and maintains Army communications and electronic equipment, approximately 40 percent of the current work load is overhaul and maintenance. New fabrication makes up the balance of the workload and is increasing. Application of cadmium surface coatings by electroplating is used during standard operations and wastes typical of cadmium plating are generated. Additionally, abrasive blasting and hand sanding generates residuals contaminated with cadmium. Because cadmium contamination is present in approximately 60 percent of the total hazardous waste generated by the depot, TOAD is seeking to replace at least part of its cadmium plating with aluminum AIVD. The AIVD system, when acquired, will be installed in a new Industrial Operations building which is currently being designed.

5.0 IMPLEMENTATION OF AIVD AT TOAD

In general, the AIVD coating process is impacted by few regulatory restrictions and generates essentially no wastes. Based on the HAZMIN benefits and on specific successes achieved by ANAD and CCAD and other military and commercial applications, TOAD Production Engineering staff determined that AIVD would benefit their operations. Review of the capital equipment acquisition process revealed the need for preparation of formal Bid Specifications, an Economic Analysis, and a Work Order.

5.1 BID SPECIFICATIONS

An equipment Bid Specification was prepared in the format specified by the TOAD Production Engineering staff. Because a significant time will lapse prior to procurement of an AIVD system, the Bid Specification

will have to be reviewed and updated/revised as necessary to reflect current conditions at the depot and any advances in AIVD technology. The Bid Specification identifies the minimum requirements for the design, manufacture, inspection, performance, and installation of an AIVD system. The specification sets minimum criteria so that technological advances are not limited. A full size chamber, 6 by 12 feet, is specified. Although smaller chambers are available and the possibility of specifying a smaller vacuum chamber was discussed with the Production Engineer, a full size system has greater flexibility in operation and throughput. Based on lessons learned at ANAD and CCAD, a cryogenic pump ("cryopump") and a computer controller are included in the Bid Specification as requirements. Standard features including air ride dollies, parts racks, and dual barrel coaters are also included. In addition to the equipment, the specifications also address provisions for technical manuals and training of operators.

5.2 ECONOMIC ANALYSIS

An Economic Analysis (EA) was prepared for implementation of AIVD at TOAD. However, all data and information required for completion of an actual economic analysis was not available. Critical information including current and projected work loads, number of parts that will be plated with the substitute coating, and waste generation rates for specific cadmium plating operations was either not available or is anticipated to change prior to implementation. Therefore, a draft EA was prepared to serve as a guide for subsequent revision when the anticipated procurement is imminent. Several significant assumptions were required for completion of the draft EA. Most significantly, the relative number of parts that would receive the AIVD coating was estimated as a percentage of the cadmium plated workload. This assumption controls the number of shifts that an AIVD system would operate, which in turn controls labor and utility costs. Similarly, the actual reduction in cadmium waste generation rates had to be estimated.

5.3 WORK ORDER

A Work Order was prepared for completion of site preparation work necessary for installation of an AIVD system at TOAD. This Work Order was prepared to facilitate reviews and planning that will be conducted by the facility engineers. The information included in the draft Work Order provides information on required space, utilities, floor loadings, etc., that will be used by the designers of the new building in planning for an AIVD system. The Work Order specifies the requirements for a "clean room", approximately 26 by 37 feet, to serve as the air conditioned AIVD plating shop. This room must have smooth (no cracks or grooves), level (to 1/4 inch in 5 feet or better) floors. Epoxy floor coating is recommended. The floor loading limit must be 1000 pounds per square foot, or greater. The air conditioning must be capable of maintaining $70^{\circ}\text{ F} \pm 2^{\circ}$ at a relative humidity of 50 percent ± 5 percent. A single 4 inch diameter PVC exhaust duct will vent the vacuum pump through a roof ventilator. This is the only air discharge. Non-contact cooling water (40 psig, $<80^{\circ}\text{F}$, 24 gpm) will be required for the pumps. Other utilities include electrical (480 V, 3 Phase, 60 Hz, 300 amp for the AIVD system and 460 V, 3 Phase, 60 Hz, 3 amp and 110 V, 1 Phase, 60 Hz, 6 amp for the blast booths), air (60-80 psig, 70 cfm for the blast booths and parts rack dollies), welding quality compressed argon and nitrogen gas. An area of approximately 44 by 37 feet will be required for the AIVD system, including the clean room, all mechanicals, and pre- and post-treatment blast enclosures.

5.4 SUBSTITUTION OF COATINGS

The substitution of aluminum coatings for cadmium coatings is controlled by the weapons or systems program office responsible for the part. Each part must be evaluated by the program office to determine if the substitute coating is acceptable. Qualification testing and acceptance process can be a time consuming undertaking.⁸ "Blanket approvals" are not typical and the approval process is carried out separately for each specific part. A specific logic chart should be developed at each location (i.e., depot) and potentially for each weapon system or parts program office/manager during implementation of AIVD coatings. The chart should be developed with input from the production engineering group, the plating shop, and the program manager responsible for the part or system. Print and assembly drawings of the part and the weapon system must be reviewed during the assessment to acquire information on tolerances and critical coatings, etc.

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**Economic Comparison of
UV/Oxidation, Anaerobic Fluidized Bed Reactor, and Granular Activated Carbon for the
Treatment of Propellant Production Wastewater Containing 2,4-Dinitrotoluene**

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Abstract

2,4-Dinitrotoluene (2,4-DNT) is used in the manufacturing process of single- and multi-base propellants at the Radford Army Ammunition Plant (RAAP) in Radford, Virginia. Slug flows of 2,4-DNT enter the wastewater stream via discharge from several batch production operations including water-dry, wet screening, and solvent recovery. The existing biological wastewater treatment plant (BWTP) receives wastewater from all operations for treatment prior to discharge into the New River under a National Pollutant Discharge Elimination System (NPDES) permit. Previous studies have indicated that the BWTP influent wastewaters contain up to 75 mg/L of 2,4-DNT. The current daily discharge limits for 2,4-DNT are 113 µg/L (average) and 285 µg/L (peak). The BWTP has had occasional problems meeting this discharge level and it is anticipated that the discharge limit may be further reduced significantly.

To address this situation, the U.S. Army Environmental Center (USAEC) has conducted a pilot-scale field demonstration project at RAAP using a UV/Oxidation and an Anaerobic Fluidized Bed Bio-Reactor (AnFBR) for pre-treating the 2,4-DNT wastewater at the point of generation (i.e., upstream of the BWTP). During this demonstration, RAAP also implemented transportable Granular Activated Carbon (GAC) adsorbers as an interim measure to pretreat wastewater as it is generated from the solvent recovery and water-dry operations. The data collected during operation of these temporary carbon units has been compiled and analyzed with the UV/Oxidation and AnFBR systems. Treatment of these wastewaters is complicated by the presence of alcohol and ether in high concentrations. These solvents interfere with the treatment efficiency of UV/Oxidation and GAC in 2,4-DNT removal while assisting pre-treatment by AnFBR. These factors were investigated during the pilot tests and based on the experimental data, a preliminary design of full-scale units for each technology was established. A life-cycle economic cost analysis for each technology was then performed to compare the relative costs of each option and it's economic return on investment.

This paper presents the conclusions of the pilot-scale demonstrations and a summary of the life-cycle cost comparison for the technologies evaluated.

Introduction

Recently, changes in production levels at the Radford Army Ammunition Plant (RAAP) coupled with increasingly stringent regulation of wastewater discharges, have resulted in the need for improved treatment of propellant production wastewaters containing 2,4-dinitrotoluene (2,4-DNT). The RAAP is a government owned, contractor operated (GOCO) facility currently operated by Alliant Techsystems, Inc. The RAAP produces a wide variety of propellants and explosives for use by the U.S. military. 2,4-DNT is used in the production of single-base propellants. This production process is conducted in a batch mode which includes operations which generate wastewater containing various concentrations of 2,4-DNT and other organics (e.g., ethanol and ether) and are discharged to the industrial sewer. An on-site biological wastewater treatment plant (BWTP) treats the combined flow of wastewater from most on-site production operations. The treated effluent is discharged from the BWTP to the New River which flows through the facility.

This discharge is regulated by the Commonwealth of Virginia under a National Pollutant Discharge Elimination System (NPDES) permit. It is anticipated that the state will significantly reduce the NPDES discharge limit for 2,4-DNT. Currently the daily discharge limits for 2,4-DNT are 113 $\mu\text{g/L}$ (average concentration) and 285 $\mu\text{g/L}$ (maximum concentration). In the past, the BWTP has occasionally discharged treated effluent that exceeded these concentrations but were within Virginia Water Quality Standards quantity limits for DNT in public water supplies based on the harmonic mean flow of the New River.

To support RAAP's efforts to address this situation, the USAEC sponsored an engineering study to identify the major sources of 2,4-DNT present in wastewater generated at RAAP, to characterize the flows and concentrations of these wastewaters, and conduct limited bench-scale testing of selected treatment technologies. This study concluded that the major contributor of 2,4-DNT load to the BWTP is the Water-Dry (WD) operation and recommended interception and treatment of WD wastewater prior to discharge from the WD tanks to the sewer to help ensure that the treated effluent from the BWTP is in compliance with the current and anticipated NPDES discharge limits for 2,4-DNT. Subsequently, the USAEC sponsored a follow-on study to demonstrate, at a pilot-scale, two treatment technologies. Ultraviolet Oxidation (UV/Oxidation) and Anaerobic Fluidized-bed Biological Reactor (AnFBR) with granular activated carbon technology were the two technologies selected for this pilot-scale demonstration based on the results of previous bench-scale work and other bench-scale work performed by USACERL. Additionally, a third technology, granular activated carbon (GAC) treatment was demonstrated at RAAP by Alliant Techsystems. The intent of these pilot-scale tests was to gather sufficient data regarding the treatment of 2,4-DNT in the wastewater that would allow scale-up to a full-scale system and perform an economic analysis to compare the costs of such systems.

Pilot Test Results and Conclusions

UV/Oxidation

A total of nine test runs were performed with the UV/Oxidation system. Four operating parameters were varied to evaluate performance of the UV/Oxidation system in terms of 2,4-DNT removal efficiency: retention time, ozone dosage, hydrogen peroxide dosage, and UV radiation intensity. The efficiency of UV/Oxidation treatment of 2,4-DNT in WD wastewater was found to

be largely dependent on the concentrations of ethanol and ether present in the wastewater. During the demonstration, this system was unable to reduce 2,4-DNT concentrations to the target limit (113 µg/L 2,4-DNT) except at very high oxidant dosages and extended residence times. However, the system consistently removed more than 65 percent of the 2,4-DNT in the wastewater. An evaluation of the flows to the BWTP is required to determine if this removal rate (i.e., 65 percent reduction) would permit the BWTP to meet anticipated discharge standards.

UV/Oxidation systems, in a wide variety of configurations to suit various process needs, are available through a number of commercial vendors. This technology has been implemented and proven effective and reliable on numerous wastewater streams. A relatively high degree of experience exists in the industry regarding the operation and maintenance of such systems.

AnFBR

The demonstration of the AnFBR system was conducted between September 12, 1994 and July 26, 1995. During the demonstration the forward flow rate was on the order of 0.4 gpm to 2 gpm. The results of the AnFBR demonstration indicate that the system is capable of achieving the target effluent quality (i.e., <0.113 mg/L 2,4-DNT). Most of the tests conducted were performed at a relatively low flow rate of 0.4 gpm (i.e., retention time of 7.8 hours). The test runs that were performed at higher flow rates (up to 2 gpm) were run for shortened periods, due to the lack of WD wastewater. Additional testing at flow rates of 4 gpm or higher would enhance the evaluation of the system to achieve the required removal of 2,4-DNT.

AnFBR technology is currently available from a limited number of vendors. Compared with UV/Oxidation, AnFBR is an emerging technology. Because the degree of documented experience with AnFBR is less than with UV/Oxidation, it would likely be more difficult to start up and troubleshoot the AnFBR system. This was evidenced by startup problems experienced during the demonstrations. Operational upsets were encountered because of complications with the inflow pump, alcohol delivery pump, pH control solution pump, and the main control system. Additionally, level probes in the nutrient and hydrogen peroxide sampling tanks were problematic throughout the study. Although the system, as tested, was computer controlled, the system required significant operator attention. As is typical of biological systems, the AnFBR system required significant time for reacclimation following upsets which can be caused by variation in influent quality, temperature, and other variables.

GAC

Subsequent to the demonstration of the UV/Oxidation and AnFBR systems, Alliant implemented the use of transportable Granular Activated Carbon (GAC) adsorbers as an interim measure to treat wastewaters generated from the SR and WD operations. This activity was implemented to reduce the 2,4-DNT load to the BWTP so that violations of the NPDES discharge limit for 2,4-DNT would not occur. The data collected during operation of these temporary carbon units was compiled and analyzed in a report submitted to USACERL. The information provided by Alliant is presented here to allow a comparative evaluation of GAC with AnFBR and UV/Oxidation.

The GAC units reduced the concentration of 2,4-DNT to an average of 0.02 mg/L in the effluent. This treated concentration is significantly less than the NPDES limit of 0.113 mg/L. The highest concentration of 2,4-DNT measured in the effluent (0.1 mg/L) also met the target discharge limit. During the time frame evaluated, a total of 260,000 gallons of SR and WD effluent were treated.

It is calculated that the GAC had adsorbed an estimated 51 lbs of 2,4-DNT. This amount is less than the projected capacity of the carbon (i.e., 72 lbs). Therefore, the holding capacity of the carbon was not exhausted during the study period.

The data indicate that the GAC initially adsorbed high levels of both alcohol and ether. These solvents were then desorbed when the influent concentrations dropped. This is evidenced by the fact that the observed concentrations of alcohol and ether in the effluent were frequently higher than the corresponding influent concentrations. However, the data does not indicate that 2,4-DNT or DAT adsorbed on the carbon was resolubilized during period of desorption of these solvents.

The system operated largely without problem. However, concerns existed regarding freezes that might occur during its use in winter months. A heater or heat jacket of some type would likely be required as a system modification to allow continual use of the GAC in sub-freezing temperatures.

Design Basis for Full-Scale Systems

Based on anticipated propellant production rates and WD cycle times, 4 gpm was selected as the flow rate design basis for a full-scale system. The design basis concentrations were selected based on the concentration levels of contaminants encountered during the pilot test demonstrations. These concentrations are: 2,4-DNT 100 mg/L average and 150 mg/L maximum; and, alcohol 300 mg/L average and 1,000 mg/L maximum. The treatment system could be expected to operate on an intermittent basis for a total of 175 days per year.

Using this design basis, the following full-scale systems were selected:

- UV/Oxidation - A system capable of providing a residence time of 960 minutes (reactor volume of 3,900 gallons), an ozone generator capable of providing 2,400 mg/L ozone, approximately 115 lbs/day ozone for a 4 gpm system, a hydrogen peroxide delivery system capable of delivering 200 mg/L (or about 9.5 lbs/day) hydrogen peroxide, total lamp power of 55 kW. The total electricity draw of the system would be about 81 kW (including the ozone generator).
- AnFBR - Two systems were considered for the full-scale application. One with a 5.2 m³ bed volume. This system provides a safety factor of 3.5 based on 100 mg/L 2,4-DNT loading at 4 gpm. The other system considered has a 1.56 m³ bed volume. This system does not provide a safety factor for treating 100 mg/L 2,4-DNT at 4 gpm.
- GAC - A system similar to that leased for temporary treatment was selected for the full-scale application. This system consists of two carbon adsorbers with total capacity of 3,600 lbs.

Economic Comparison of Treatment Alternatives

Cost estimates prepared for each of the three treatment alternatives evaluated in this study were calculated based on ten years of operation at 4,000,000 pounds of annual propellant manufacture and with an assumed interest rate of 7 percent. A graph showing the cumulative annual costs for ten years of operation is shown in Figure 1.

The costs calculated for the systems selected as potential candidates for full-scale application were as follows:

	UV/OX	1.56 m ³ AnFBR	5.2 m ³ AnFBR	GAC
Capital Cost	\$155,000	\$176,500	\$226,500	\$6,600*
Annual Operating Cost	\$22,300	\$10,900	\$14,250	\$80,500
Annual Operating Cost per 1,000 gallons	\$28	\$14	\$18	\$101
Present Worth (10 years at 7%)	\$311,400	\$252,900	\$326,500	\$571,800
Equivalent Uniform Annual Cost (10 years at 7%)	\$44,350	\$36,000	\$46,500	\$81,400

* - Initial lease cost of the system

An analysis was performed to gauge the sensitivity of the economic analysis to the amount of propellant manufactured per year. A comparison of the cumulative operating costs over ten years for each alternative at annual propellant manufacture rates of 2,000,000 lbs and 6,000,000 lbs, respectively, is shown in Figures 2 and 3.

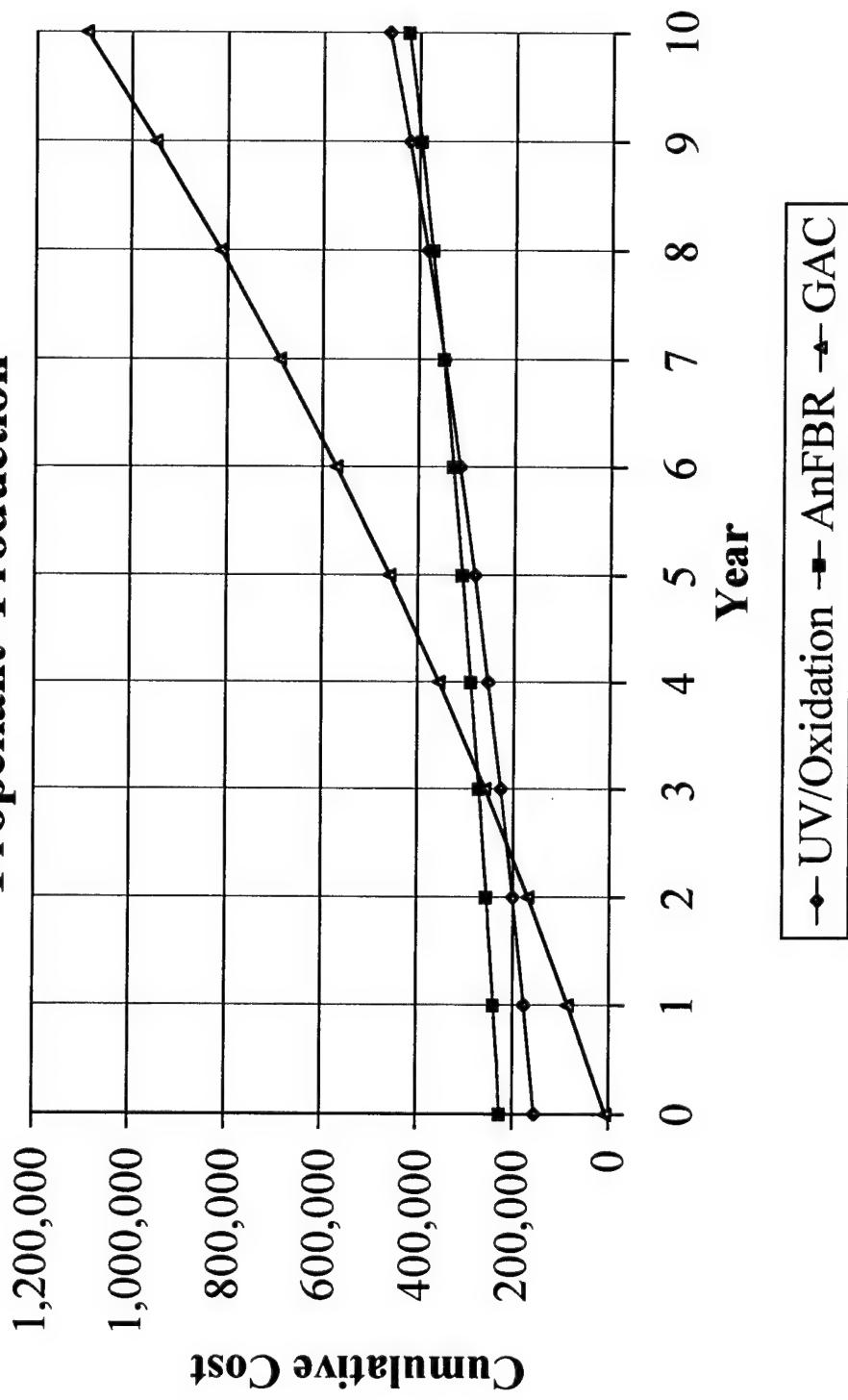
Based on the sensitivity analysis presented above, the selection of a system to be implemented at RAAP is dependent on both the amount of propellant likely to be manufactured per year and the length of time that manufacturing rate will be sustained. The difference in operating costs between the UV/Oxidation and AnFBR systems stem primarily from the number of expected operating days per year and is reflective of the fact that the UV/Oxidation system is capable of being shutdown for extended periods of time without the need for operator attention. Thus, the UV/Oxidation system is more cost effective for lower rates of propellant manufacture (i.e., lower volumes of wastewater generated per year). The AnFBR system requires continuous operator attention even in periods when WD wastewater is not generated. Furthermore, the AnFBR system must be fed supplemental alcohol during periods when wastewater is not available to maintain a viable microbial population in the reactor. Thus, increased propellant manufacture rates (and, hence, increased wastewater volumes generated) favor the economics of operation for the AnFBR system.

Conclusions

- All three technologies were shown to be capable of treating 2,4-DNT to the desired effluent levels.
- UV/Oxidation is well suited for treatment of intermittent flows. The system can be shut down and restarted quickly and as required. UV/Oxidation was the most susceptible to changing alcohol levels.
- GAC is a proven and readily implementable technology. It has been demonstrated to be effective in removing 2,4-DNT from WD wastewater at RAAP.
- The AnFBR system required significantly more effort to set up and operate than the UV/Oxidation system. An acclimation period is required at start-up or after significant changes or upsets in operating conditions.

- The AnFBR consistently reduced concentrations of 2,4-DNT to levels below the target of 0.113 mg/L.
- An AnFBR system would have to be operated continuously to maintain a viable biomass and to avoid lengthy start-up times.
- GAC system has the lowest cumulative costs for the first 2 to 3 years of operation when compared to UV/Oxidation and AnFBR.
- Changes in the concentration of 2,4-DNT present in WD wastewater significantly impact the cost of treatment by GAC.
- Over longer periods, UV/Oxidation is estimated to be the most cost effective alternative at low propellant production rates and AnFBR is more cost effective at current and higher production rates.

Figure 1
Ten-Year Costs Based on 4,000,000 lbs of
Propellant Production



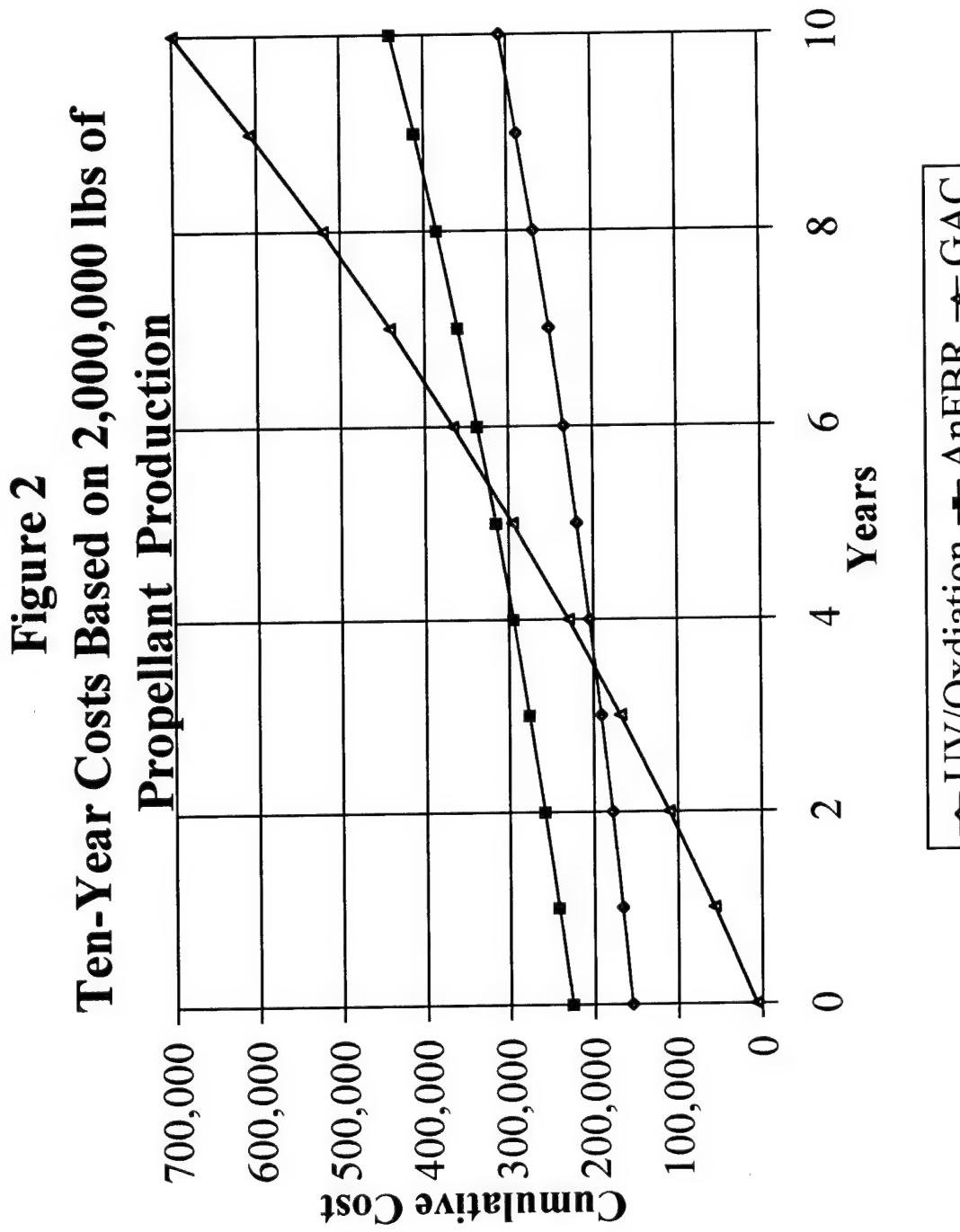
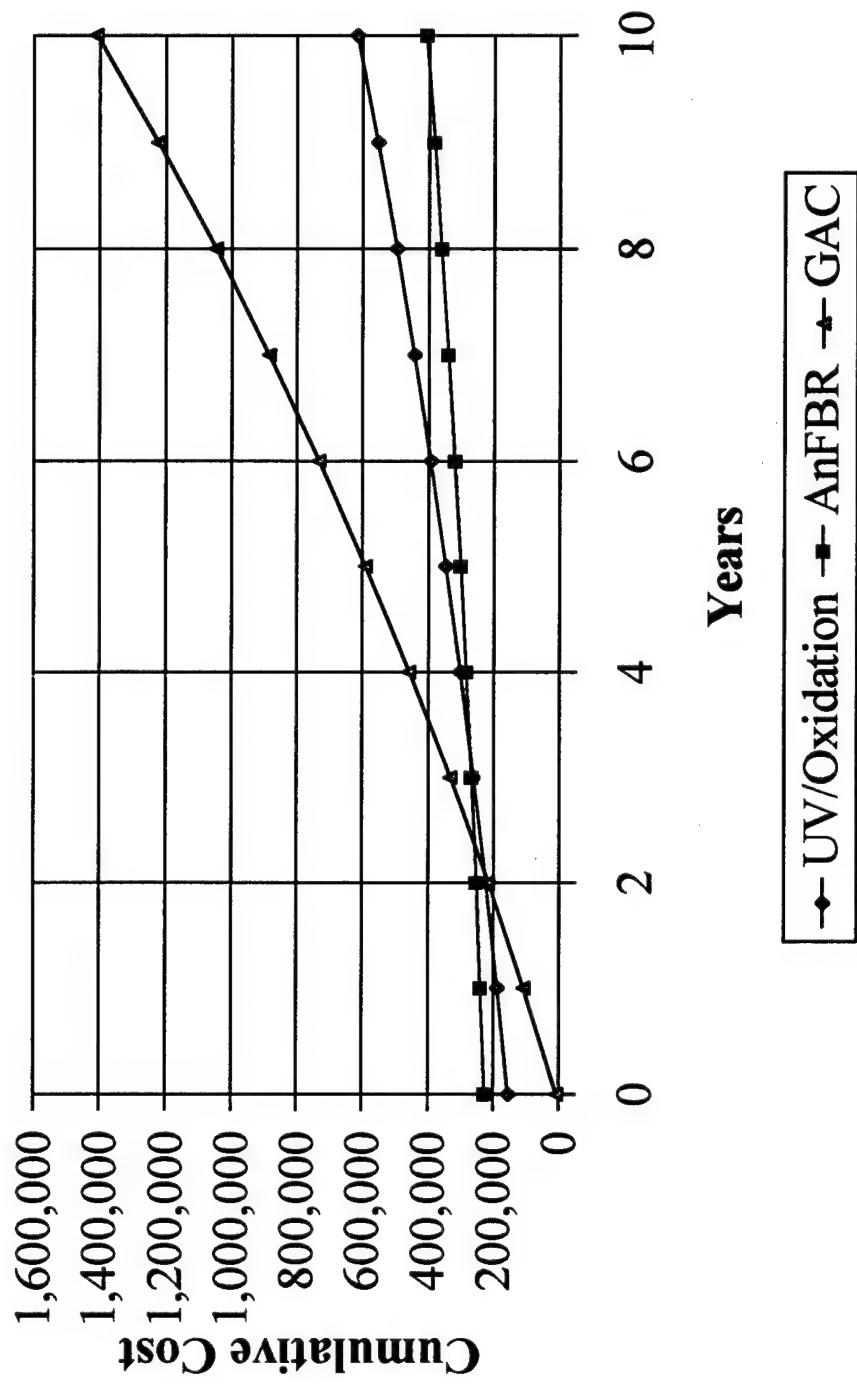


Figure 3
Ten-Year Costs Based on 6,000,000 lbs of
Propellant Production



PROTECTIVE COATING ANALYSIS

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ABSTRACT

As a National Center for Energetics, the Indian Head Division, Naval Surface Warfare Center (IHDIV, NSWC) is committed to providing quality products in support of the Fleet. In concert with this effort, the AEPS/PAD Engineering and Production Divisions provide life-cycle support for various Navy Aircrew Escape Propulsion Systems (AEPS) devices used in aircraft. This cradle-to-grave philosophy has led to a strive for technical excellence as well as environmental responsibility. To support these goals, the AEPS/PAD Engineering and Production Divisions recently performed extensive testing of various low Volatile Organic Compound (VOC) coatings for use on its various (AEPS) devices. Testing was performed to identify an environmentally compliant coating with improved durability.

Coating application and evaluations conformed to American Society for Testing and Materials (ASTM) and Military specifications and were accomplished in two phases. Phase I subjected twenty-seven coating systems to a battery of qualitative and resistance properties testing. The coatings were derived from an exhaustive family of epoxies, latex, urethanes, calcium sulfonates, vinyls, and alkyds. Upon completion of Phase I, it was determined that polyamide epoxies and polyurethanes exhibited the qualities sought. The compliant coatings' performance exceeded that of the baseline significantly, application was easier, and results correlated well with published field testing. Initial difficulties were overcome concerning the application, clean-up, testing, and health hazards of the low VOC paints. Complicated air sampling for the determination of isocyanates and polyisocyanates was conducted to certify that levels were below all established limits in this country in an effort to protect the worker. Six of the best performing primers and paints were selected for more complex and stringent testing in Phase II. The six systems were selected on the basis of their ratings after evaluation using a weighted scoring system. Heavily weighted characteristics were those that exhibited the greatest potential to impact worker health, paint performance, and the environment. Phase II resulted in the selection of a polyurethane topcoat and reduced the field of primers to three. The testing demonstrated that the polyurethane coating exhibited excellent adhesion and great resistance to lifting and chipping in addition to polyurethanes' well-known attributes of chemical and UV resistance, flexibility, and high gloss retention. This paper discusses the development, test methods, results, and lessons learned from Phases I and II of the Protective Coating Analysis performed at the Indian Head Division, Naval Surface Warfare Center.

1. INTRODUCTION

Over the years, environmental regulations have become more stringent and expansive in the areas that they cover. To control air pollution, restrictive environmental regulations encouraged the development of paint formulations that generate less air emissions. These coatings were entering the market with little research to support manufacturer's claims and there were limited studies for comparisons. While the Maryland Department of the Environment (MDE) proposed further restrictions for metal coatings, IHDIV, NSWC identified a need to establish a more durable coating due to discrepancy reports received concerning corrosion on AEPS units. These factors contributed to the decision to conduct an evaluation prior to selecting a replacement coating. The primary objective for these assessments was to compare new coating technologies that meet proposed environmental regulations in Maryland and exhibit performance exceeding that of the current coating system.

2. BACKGROUND

The purpose of the Protective Coating Analysis program stems from two concerns: environmental compliance and durability. Impending environmental regulations stipulated that all paints utilized for metal protection have low Volatile Organic Compound (VOC) levels by May 1996, with the exception of maintenance coatings. The maximum allowable VOC content in the Maryland legislature's draft was 420 g/L (3.5 lb/gal). The paints that IHDIV, NSWC were using on AEPS devices exceeded the allowable VOC level. If a replacement coating was not found, production of AEPS devices could not be maintained. Corrosion reports from the Fleet further compounded the issue by adding a durability concern.

AEPS devices are typically found on ejection seats of various aircraft supporting the national defense. These units have various amounts of explosives and propellants in them and are critical in the ejection sequence. AEPS items are "man-rated" which means that failure may cause a loss of life. Thus, when AEPS devices show extensive corrosion, they are rejected and disposed. AEPS coatings must maintain their integrity in rugged environments for up to seventeen years. These conditions consist of temperature extremes from -65°F to 165°F, extreme humidity, and corrosive environments found on aircraft carriers.

3. EVALUATION PROGRAM

Phase I consists of applying the selected low VOC coating systems to test panels for both qualitative and resistance testing and evaluation. The objectives of Phase I were to identify environmentally compliant coatings that exceed the performance of the currently used system, identify alternate coating systems to utilize for production, and select six systems for further validation. Phase II was developed to further reduce the field of candidates while validating Phase I test results. A weighted scoring system devised to meet the above-mentioned objectives was employed for all test panel evaluations. Phase III testing shall subject the three best coating systems from Phase II to identical tests utilizing various substrates found on AEPS devices. Finally, these panels shall be exposed to weathering tests.

4. PHASE I

Prior to any testing, an extensive literature search and a review of various government and industry testing was performed. The intent of this research was to identify coatings that could work well in the unique AEPS operating environment and meet program concerns. These efforts identified twenty-seven coating systems that claimed to fit the criteria. The coatings were from various urethane, epoxy, vinyl, alkyd, latex, and calcium sulfonate families. The original coating system that served as the baseline for comparison consisted of a polyamide epoxy primer topcoated with an acrylic lacquer complying with MIL-P-23377F and MIL-L-81352A, respectively.

4.1 METHODS

A flat 4130 steel substrate was utilized because it is the dominant material used on AEPS motors. Since the original application does not allow any alteration to the plated surface (i.e., sanding or blasting), each panel was cleaned and wiped down with solvent per ASTM D609-95. The current coating system served as the control sample. All coatings were applied with High Volume Low Pressure (HVLP) spray guns. Application, recoat time, and dry times were per the individual manufacturer's recommendations. Since one of the objectives was to meet or exceed current performance levels, the majority of the tests were derived from the acrylic lacquer's test specification (MIL-L-81352A). The remainder of the tests were taken from MIL-P-83126A, the specification for the design of AEPS devices, in order to ensure that the coatings could withstand the AEPS operating environment. Each of the coating systems were subjected to qualitative and resistance properties testing. All tests were performed in triplicate, such that three panels were utilized per paint panel, per test. The following gives a brief description of each test and its purpose:

4.1.1 QUALITATIVE TESTS

Working Properties - MIL-L-81352A. Primer is applied to each panel and allowed to dry. Two coats of paint are then applied and allowed to air dry for twenty-four hours. After the drying period, the paint is visually inspected for cobwebbing, running, sagging, streaking, blushing, orange peeling, and hazing. The purpose of the working properties test is to evaluate surface appearance and working (spraying and drying) properties of the paint.

Self-lifting Properties - MIL-L-81352A. Primer is applied to each panel and allowed to dry fully. Two coats of paint are then applied to the primer with different drying intervals between each coat. Hence, the purpose of this test is to evaluate intercoat adhesion of the system's topcoat and evaluate its tolerance to drying interval deviations from the recommended interval.

Surface Appearance - MIL-L-81352A. Panels from the working properties test are utilized for this test. This test is similar to the working properties test but more stringent in that the surface of the coating is examined under a magnification of 10 to 15 diameters.

Primer Lifting - MIL-L-81352A. Primer is applied to panels and allowed to dry at different intervals prior to application of two coats of paint. The purpose of this test is to evaluate adhesion of the primer to the substrate and rate its tolerance to drying interval variations.

Coating Anchorage - Primer and paint are applied to each panel. After air-drying for one week, the coating is subjected to a knife test (FED-STD-141C, Method 6304.1). This test indicates the flexibility of the coating, the ribboning ability of the coating, and dry-knife adhesion.

Adhesion (wet) Tape Test - FED-STD-141C, Method 6301.2. Primer and paint are applied on panels. Each panel is air-dried for one week and then partially immersed in distilled water for twenty-four hours. After removal from the water, panels are wiped dry. A stylus is used to impart two straight lines one inch apart along the width of the immersed portion. Subsequently, a one inch strip of masking tape is applied perpendicular to the lines and removed in one brisk stroke. The purpose of this test is to evaluate intercoat and substrate adhesion.

4.1.2 RESISTANCE PROPERTIES TESTS

Water Immersion - FED-STD-141C, Method 6011. Primer and paint are applied to each panel and allowed to air-dry for one week. Panels are then immersed in distilled water for twenty-four hours. This test was performed in conjunction with the tape test. The purpose of this test is to evaluate the coating's integrity when subjected to prolonged immersion.

Temperature Cycling - MIL-P-83126A. Primer and paint are applied to each panel and allowed to air-dry for one week. Panels are then cycled three times from -65°F to 160°F. The purpose of this test is to evaluate performance of the coating during temperature transitions and at prolonged temperature extremes.

Humidity Test - MIL-P-83126A. Primer and paint are applied to each panel and allowed to air-dry for one week. Panels are then stored at a temperature of $120^{\circ} \pm 5^{\circ}\text{F}$ and 100% humidity for ten days. The purpose of this test is to evaluate the coating's ability to withstand humid environments.

Salt-spray Test - MIL-STD-810, Method 509. Panels from the humidity test are utilized for this test. Panels are subjected to 168 hours of salt-spray in a 20% salt solution. The purpose of this test is to demonstrate the coating's ability to withstand corrosive environments.

4.2 PHASE I RESULTS

Three main objectives were accomplished during Phase I:

- (1) Coatings were identified that exceeded the performance of the baseline sample.
- (2) Six systems were selected for further validation as shown in Table 1.
- (3) Viable alternatives were put into place to maintain production of AEPS units. These coating systems, marked with an asterisk in Table 1, were chosen from the top six because they performed most consistently during testing.

TABLE 1. PHASE I SELECTED COATINGS

PRIMER	TOPCOAT
MIL-P-53030 *	MIL-C-85285B *
MIL-P-85582 *	MIL-C-85285B
Zinc-rich epoxy	TT-P-2756 *
MIL-P-53030	Fluoropolyurethane
Moisture-cure (MC) MIOZinc	MC Urethane
Calcium sulfonate	MIL-C-85285B

In comparing results with other government and private agencies, it was discovered that Phase I results balanced well with previously performed testing and actual use by the New Hampshire Department of Transportation (DOT), North Carolina's DOT, Naval Aviation Depots at Cherry Point, NC and Jacksonville, FL, Alberta Transportation and Utilities, and Aerojet Propulsion. Also, results correlated well with MIL-F-7179G which was developed for the protection of aerospace weapons systems.

5. PHASE II

A complete test plan, similar to that used for Phase I, was developed and executed. The testing in Phase II was designed to narrow the field of top performers from paints selected from Phase I and validate Phase I test results. Additional testing introduced here includes resistance to cyclic corrosion testing, chipping, and solvents.

5.1 METHODS

A recommended practice is to configure accelerated test models so they imitate the actual objects to be coated. Test results utilizing this emulation of actual shapes have been shown to more closely replicate actual field performance. This reasoning led to the use of non-flat test panels for this phase: Each panel had a 1/2" x 1" "U"-shaped channel tack welded near the bottom. This channel simulates the curves found on AEPS devices while the edges serve to test the relative ability of the coating to adhere to non-continuous surfaces.

5.2 ADDITIONAL TESTS

The humidity test was replaced with a method corresponding to ASTM 2247 because of a wider acceptance in industry. The panels subjected to the humidity test were photographed when removed from the chamber, however, they were placed back into the chamber within the hour to subsequently undergo the cyclic salt-fog test. This quick transition is required per MIL-P-83126A.

A cyclic corrosion test replaced the continuous exposure salt spray test performed in Phase I. This decision was based on simulation logic and past research. Since actual atmospheric exposures include both wet and dry conditions, it seems natural to model accelerated laboratory tests after a cyclic environment. A dry-off period makes this test more strenuous because it gives oxygen an opportunity for adsorption, resulting in the formation of oxide layers¹. This action occurs after the humidity has deposited a condensed film that sets up an electrical potential between the iron and other materials in the metal, thus causing corrosion. Research indicates that with cyclic corrosion tests, the relative corrosion rates, structure and morphology are more similar to those seen outdoors². Consequently, cyclic corrosion tests usually provide a closer correlation to outdoor exposure than conventional salt spray tests. This has been demonstrated in numerous tests and is becoming more widely accepted³. A cyclic test corresponding to ASTM G85 ANNEX 5 was used in Phase II because it simulated the conditions AEPS devices are exposed to. This test consists of salt-fog, humidity, and dry-off cycles.

Chip resistance was a primary concern for this effort because chipping was reported along with the corrosion in discrepancy reports. Chipping occurs when AEPS devices are placed on top of sharp objects during handling and routine maintenance operations. Phase II incorporated ASTM D3170 which provided a method to test and evaluate test panels for chip resistance. This test projects road gravel at the painted surface at a pressure of seventy psi for ten seconds.

5.3 PHASE II RESULTS

Two primary objectives were achieved during Phase II: (1) Phase I test results were validated, and (2) the field of candidates was reduced to one topcoat and three primers. The difference between all six coatings' performance was imperceptible after temperature cycling, tape, and primer lifting tests. The best performing paints correlated again with MIL-F-7179G. The topcoat corresponding to TT-P-2756 was eliminated due to poor chipping performance and pinholing. The fluoropolyurethane was removed from further consideration due to poor chip and cyclic salt-fog resistance and the need for a highly volatile thinner. The moisture-cure topcoat and primer also required a highly volatile thinner and there were application problems related to their viscosity. The calcium-sulfonate primer performed superbly in the cyclic salt-fog, however, failure to maintain intercoat adhesion with an ideal topcoat caused its removal from further testing.

The topcoat, MIL-C-85285B, was selected as a permanent replacement coating for AEPS devices following these failures. Reducing the number of topcoats to one shall reduce the variables in Phase III and ensure the validity of the final primer selection. The remaining primers to be further evaluated are water-reducible polyamide epoxies. The MIL-P-53030 is lead and chromate free while primer meeting MIL-P-85582 uses barium chromate in its formulation. The zinc-rich epoxy primer performed very well after initial difficulty was met reducing its viscosity.

6.0 ANALYSIS

Since the majority of results were qualitative versus quantitative, a weighted scoring system was utilized in evaluating results. This method involves the defining of classifications for various types of "defects" and then weighting each type. Weights were assigned based on the impact each characteristic would have on AEPS application, service life, maintenance, environmental concerns, and worker safety. This system is based on a modified control chart used to evaluate quality. Table 2 details the weighting scheme for each characteristic evaluated as seen below:

TABLE 2. Q-CHART WEIGHTING SCHEME

QUALITATIVE TESTS (Phase I)		QUALITATIVE TESTS (Phase II)	
<u>Primer</u>	<u>Weight</u>	<u>Primer</u>	<u>Weight</u>
Intercoat adhesion	1.00	Intercoat adhesion	1.00
Coating anchorage	2.00	Coating anchorage	2.00
Tape test	2.50	Dry tape test	2.50
Primer lifting	3.00	Tape test	3.00
Thinning	3.00	Primer lifting	4.00
<u>Top Coat</u>		<u>Top Coat</u>	
Working properties	0.50	Working properties	0.50
Surface appearance	1.00	Surface appearance	1.00
Water resistance	2.00	Water resistance	2.00
Self-lifting	2.50	Resists self lift	2.50
Thinning	3.00	Thinning	3.00
RESISTANCE TESTS (Phase I)		RESISTANCE TESTS (Phase II)	
<u>System</u>	<u>Weight</u>	<u>System</u>	<u>Weight</u>
Water immersion	2.00	Water immersion	2.00
Temperature cycling	2.00	Temperature cycling	2.00
Humidity	3.00	Salt-fog/Humidity	5.00
Salt-spray	5.00	Chipping	4.00
		Solvent	3.00

The weighting scheme above was used to create a Quality Score Chart or Q-Chart.⁴ The Q-Charts for Phases I and II are shown in Figures 1 and 2 respectively. To arrive at a final score for each coating system, each characteristic weight was multiplied by 0.5, 1.0, 2.0, or 3.0 signifying poor, fair, good, or excellent performance respectively. For example, the medium used for thinning corresponded to these ratings based on whether the coating used a solvent (0.5), other (1.0), water (2.0), or no thinner (3.0). This value was then multiplied by the weight given to the characteristic "Thinning". Of the qualitative properties, thinning was given the most weight due to worker safety and environmental regulations. The next most important qualitative properties are primer lifting and self-lifting. These properties were weighted accordingly due to the important role that primer and intercoat adhesion play in a coating's service life and performance. Salt-spray was weighted the greatest under resistance properties since the most rigorous coating environment is a corrosive one. Additionally, it has been historically recognized that salt-spray tests are the most severe tests of coating integrity.

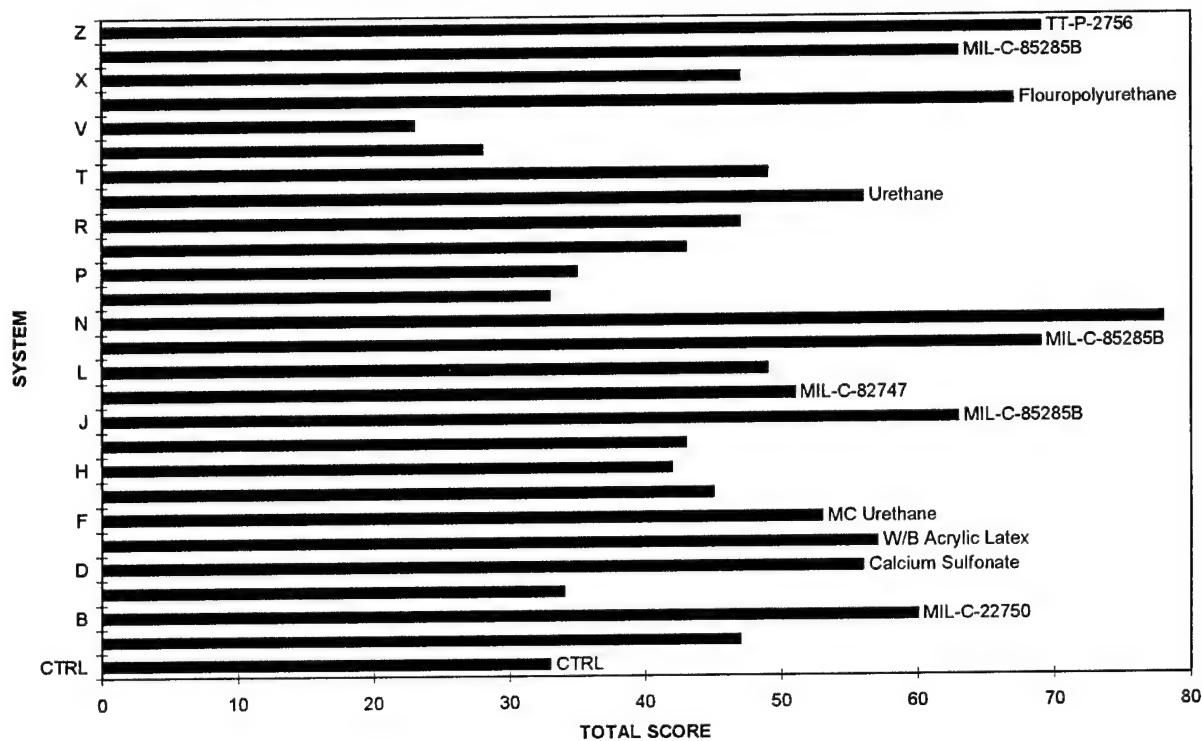


Figure 1. Phase I test results. Q-chart depicts weighted scores of each coating system.

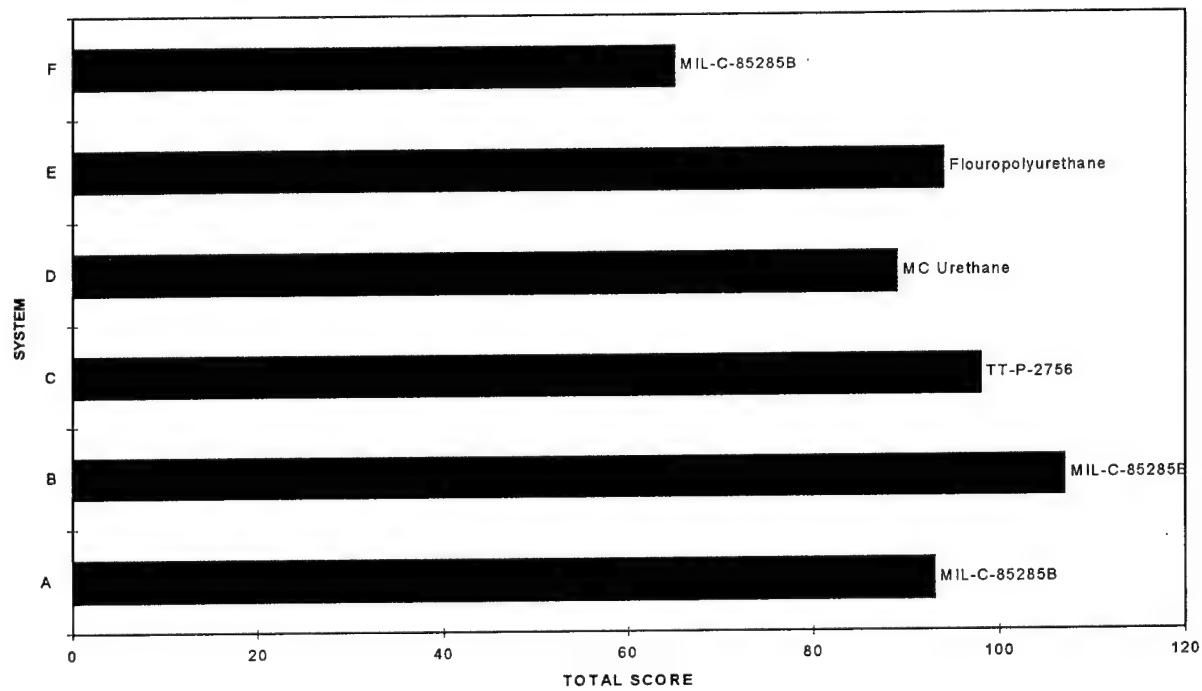


Figure 2. Phase II test results. Q-chart depicts weighted scores of each coating system.

7.0 LESSON LEARNED

Throughout execution of the program, various lessons were learned. Test plans were modified as necessary to incorporate these changes in order to refine the test methods. The following details the lessons learned throughout Phases I and II:

- (1) A procedure was provided for sealing the panel edges. This was done in order to prevent corrosion that formed at the edges during resistance tests from proliferating to the rest of the panel.
- (2) The temperature in the paint booth was recorded. Different temperatures can affect the application and drying of the coatings and this helped to control this variable.
- (3) The recommended cleaner, thinner, mixing ratio, viscosity, dry times, and thickness were recorded on the evaluation sheets. Recording this information helped the application of paints run much more efficiently and provided a reference during analysis.
- (4) When the paint sprayed inadequately, the first panels were not covered uniformly. Therefore, the applicator sprayed a section of scrap metal until it applied consistently.
- (5) Dry film thickness was measured in order to ensure coatings were applied per manufacturer's recommendations.
- (6) The engineer was required to be present during mixing and first application. This resulted from an incident during which too much solvent was added to the coating, thus causing the coating's VOC level to exceed the maximum allowable level. One of the criteria examined in Phase I was how simple the coating was to work with out of the containers. Applicators were instructed to make adjustments as necessary to get an adequate spray while staying below the VOC limit, however, oversight was not in place for three days during Phase I.
- (7) When urethane coatings first showed positive results, the isocyanate issue was examined. This examination indicated that safe isocyanate exposure levels were neither well documented nor fully understood. One of the primary manufacturers, Miles Inc., has established guidelines and the Occupational Safety and Health Administration (OSHA) has set a very conservative limit for the hexamethylene diisocyanate (HDI) monomer. Industrial hygienists from the National Naval Medical Center in Bethesda, Maryland conducted complex air sampling for HDI-Polyisocyanate and the HDI-Monomer in a spray paint booth at IHDIV, NSWC. The levels for each were found to be below the Miles Guideline Limit of 1 part per million (PPM) and the OSHA's Short Term Exposure Limit (STEL) of 0.18 PPM respectively. Therefore, approval was granted to operate with a combination respirator as described in Table 3 along with other related test equipment.

TABLE 3. TEST EQUIPMENT

EQUIPMENT	MANUFACTURER	MODEL
Paint spray guns	Air-Verter	AV-001MG (#5cap,#12noz)
Viscosity cup	Zahn	Signature Series S90, #2
Masking tape	3M	Code No. 250
Gloves, protective	Ansell Edmont	Neolatex
Combination filter/respirator	Mine Safety Appliances Co.	Comfo II w/GMA-H Cart.
Rubber covered roller	Paul N. Gardner Company	Meets Fed. Test Std. 6301.2
Chip resistance test chamber	Q-Panel Company	Gravelometer ASTM D3170
Coating thickness gage	DeFelsco	6000-2
Standard salt-fog chamber	Singleton	32
Temperature recorder	Honeywell	AR100
Humidity chamber	Envirotronics	EH125-2
Temperature recorder	Honeywell	455X21
Thermal cycling chamber	Webber	WF40-100
Temperature recorder	Honeywell	AR100
Environmental test chamber	Atotech USA Inc.	CCT-P20

CONCLUSION

The development and execution of a customized test plan is an effective method to evaluate coatings for specific applications. The actual testing of products gave results that often conflicted with the coating manufacturer's claims, but also was essential to making a replacement decision. That decision, based on the research and experimental results herein, was also bolstered by applying, testing, and evaluating the products on-site. This enabled the applicators and test personnel to become intimate with the coatings while providing a high level of control over the exposure conditions endured by the test panels. These factors contributed greatly to a high level of confidence in this analysis and the replacement coating selected for AEPS devices.

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WASTE ACID DETOXIFICATION AND RECLAMATION

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ABSTRACT

A prototype Waste Acid Detoxification and Recovery System (WADRTM), originally developed by the Pacific Northwest National Laboratory (PNNL) for Tinker Air Force Base, was tested at the Watervliet Arsenal in Watervliet, New York. The unit demonstrated the ability to concentrate waste acids produced by plating operations at the Arsenal so that they may be recycled. Currently, waste acids at the Arsenal are not concentrated enough to be recycled and must be disposed of. The WADRTM unit typically produced recycled acids at a concentration 8% higher than the incoming waste acid allowing the acid to be recycled back to process. Economic analysis on the installation of the WADRTM system at the Arsenal indicates that over \$100,000 per year may be saved over the current method of waste acid handling.

INTRODUCTION

Large quantities of metal-bearing spent acids are produced by electroplating, surface finishing, and chemical milling/dissolution operations common to the Department of Energy (DOE) and the Department of Defense (DOD). The intent of this study was to provide initial data to prove the efficacy of using a prototype system developed by the Pacific Northwest National Laboratory (PNNL) to recover and recycle such spent acids. The system tested is termed the Waste Acid Detoxification and Recovery System (WADRTM).

The Watervliet Arsenal, located in Watervliet, New York, has a waste stream of concentrated acids that is generated by the chrome plating line. The Arsenal has been asked by regulators to address this highly reactive and low pH waste. The WADRTM system was uniquely suited to handle this waste, using a combination of proven methods with advanced materials.

The prototype WADR™ system was originally developed and tested for Tinker Air Force Base, but refurbishments in the plating shop at Tinker AFB prevented the system from being installed. The system was subsequently transferred to the Watervliet Arsenal for initial testing at the chrome plating line and permanent installation at the vessel plating line. This report describes the tests conducted, the operability of the system and its effectiveness.

PROCESS DESCRIPTION

The WADR™ unit, as manufactured by Pacific Northwest National Laboratories (PNNL), is essentially a batch vacuum distillation unit. Major components of the system include a reboiler tank, steam heated reboiler, vacuum column, water-cooled condenser, condensate tank, and other support equipment. The unit also came equipped with a crystallizer for removing accumulated heavy metal salts, but this was not used during the demonstration. The use of fluoropolymer liners reinforced with thermosetting plastic makes the WADR™ system capable of handling the most highly reactive solutions. A block-flow diagram is shown in Figure 1 (all components are not shown).

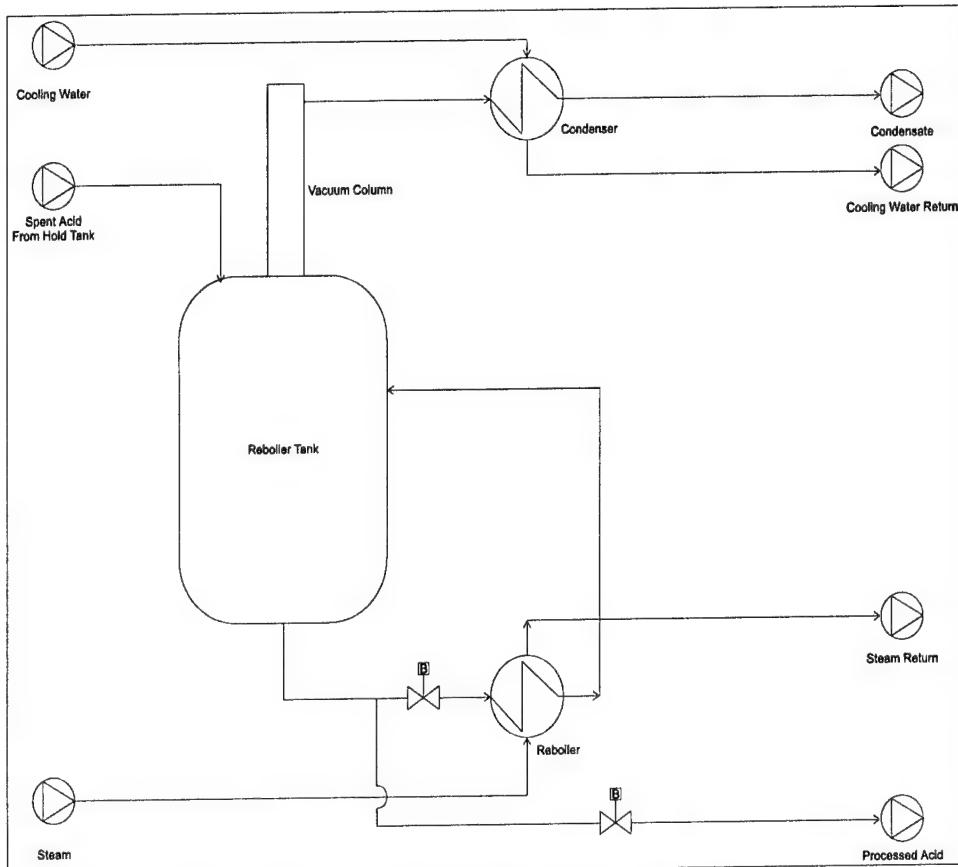


Figure 1: Block-flow Diagram of WADR™ System - Batch Distillation

Spent acid, diluted during manufacturing and containing iron contaminants, enters the system from a 3400 gallon holding tank in 200 gallon batches. The acid is concentrated until the boiling point temperature reaches a temperature consistent with an adequately dewatered acid solution. At that point the batch is removed from the reboiler tank and returned to the holding tank used in manufacturing. The system is placed under vacuum to lower the boiling point of waste acid to be recycled. Lower boiling points achieved through placing the system under a vacuum, allow for longer equipment life and lower energy costs.

EXPERIMENTAL

The WADR™ system was operated on six separate occasions to recycle manufacturing acids. The mode of operation in each case was the following:

- 1) A sample from a 3400 gallon holding tank was taken and assayed for Fe, acid A, and acid B. These concentrations were used as "initial" values.
- 2) The WADR™ system was charged with 200 gallons of metal-bearing, dilute acid solution from the holding tank.
- 3) The WADR™ system was operated until the boiling point of the charge had reached a temperature consistent with recycled acid.
- 4) Upon achieving an adequate boiling point, WADR™ operation was halted and a sample was taken from the batch tank. This sample was assayed for Fe, acid A, and acid B. These concentrations were used as "final" values.
- 5) The concentrated charge was returned to the 3400 gallon holding tank.
- 6) A sample was taken from the holding tank after the addition of the distilled charge and assayed for Fe, acid A, and acid B.

Samples were collected in HDPE containers and analyzed within 7 days. Acid samples were analyzed via titration and Fe concentrations were analyzed by Inductively Coupled Plasma (ICP). Steam consumption was determined by valving and pipe sizes. Cooling water consumption was determined by valving and pipe sizes. Electrical demand on the system was determined by calculation based on loadings marked on supporting equipment.

RESULTS

The results obtained during the demonstration are shown in Table 1. Acid content in the processed 200 gallon batches was raised 8% for acid A and 8% for acid B. Iron contents were also raised, on average, from 2.8 to 3.4 ppm. Processing times for 200 gallon batches averaged 12 hours. During this time, 220 lbs of steam were used, 1320 gallons of cooling water, and 30 kW-Hr of electricity were used. Data from Table 1 was used to calculate concentration factors. The data obtained on December 7th was not used in calculations, because this represents a 1 hour processing time that proved to be insignificant. Figures 1 and 2 express the results graphically.

Table 1: Results Expressed as a Percentage of Specification

Date	Gallons Processed	Initial Acid A	Initial Acid B	Initial Fe	Conc. Factor	Max Outlet Temp	Final Acid A	Final Acid B	Final Fe
16-Sep	200	94.01%	92.78%	-	7%	250	100.59%	99.27%	-
3-Oct	200	95.00%	98.27%	-	8%	250	102.60%	106.13%	-
18-Oct	200	95.03%	98.54%	2.60	10%	260	104.62%	108.91%	4.00
16-Nov	200	94.56%	98.98%	2.90	8%	257	102.49%	105.69%	3.10
17-Nov	200	95.62%	99.27%	2.90	8%	-	104.14%	107.30%	3.00
7-Dec	200	96.80%	103.80%	0.50	0%	275	96.80%	103.65%	0.80

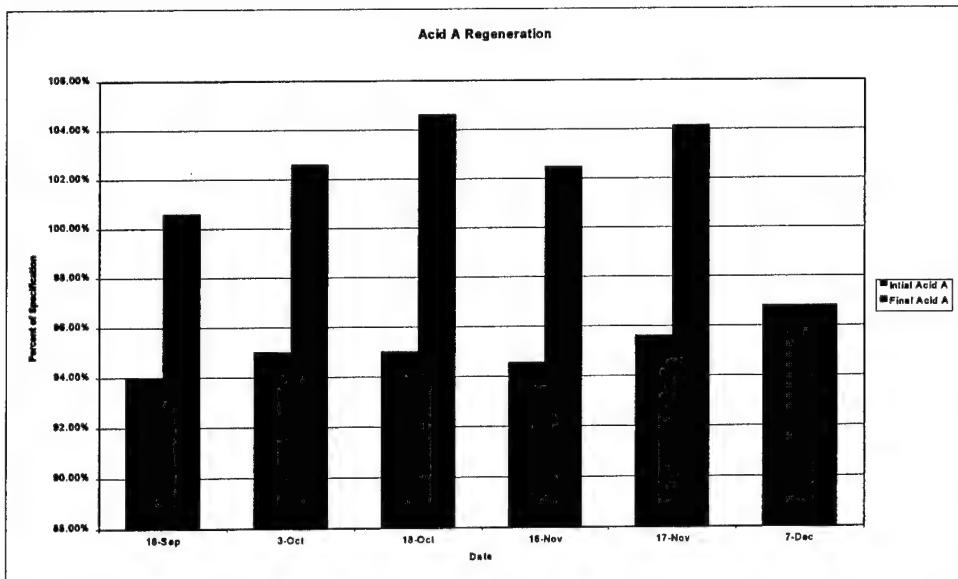


Figure 2: Acid A Concentration

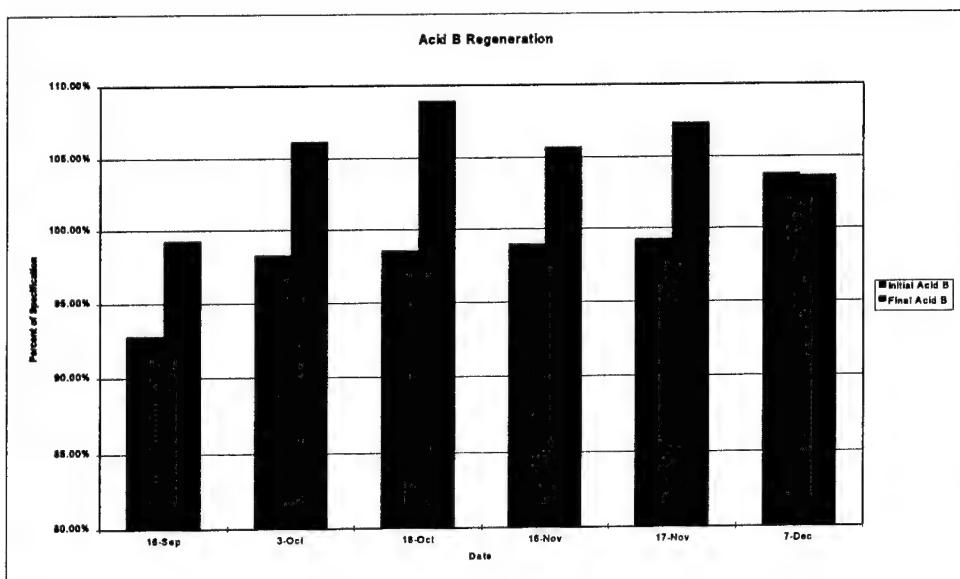


Figure 3: Acid B Concentration

DISCUSSION

A rough economical analysis can be performed on the system as tested. Typically during periods of high output, the 3400 gallon acid holding tank would have to be emptied and recharged with fresh solution. Normal levels of production activity dictate that this recharging operation be carried out 4 times a year on two 3400 gallon tanks. The cost of this operation amounts to \$193,528 per year which includes material as well as disposal costs. By using the WADR™ unit the acid can be recycled. Using the average concentration factor found during testing (8%), acid additions can be limited to \$15,958 per year and disposal costs to \$9,828 per year. Adding in the cost of utilities to operate the WADR™ unit this figure becomes a total cost of \$27,576 per year. This represents a savings to the arsenal of over \$165,000 per year. When this savings

is discounted to net present value terms using a rate of 4.8% with the initial cost of the WADR™ unit set at \$200,000 and an expected machine life of ten years, annualized savings amount to \$109,000 over the present operation.

Using the same economic model it can be seen that the total net savings realized by the installation and operation of a WADR™ unit at the Watervliet Arsenal is heavily effected by the concentration factor achieved during processing. Figure 4 shows the relationship between the concentration factor and net present value savings over a ten year life span. It can be seen that the savings realized by utilizing a WADR™ system levels off at a concentration factor around 8%.

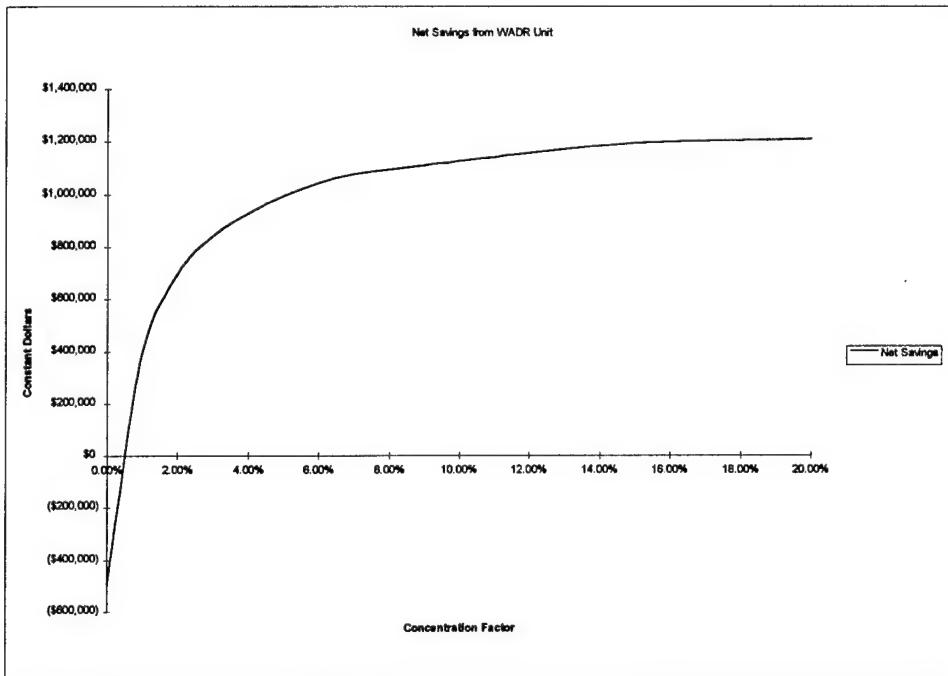


Figure 4: Savings as Related to Concentration Factor

In addition to the importance of the concentration factor in determining the economic viability of the WADR™ system, waste throughput is also a concern. Figure 5 shows the effect that waste throughput has on the economic viability of the system. Each change-out represents one 3400 gallon acid tank. During time of normal manufacturing activity the Arsenal will require 8 change-outs to maintain the acid tanks within concentration specification, resulting in an annual savings of around \$100,000. At lower manufacturing levels, annual savings drop off in a linear fashion. With just four change-outs per year a savings of only \$40,000 will be realized over a 10 year equipment life.

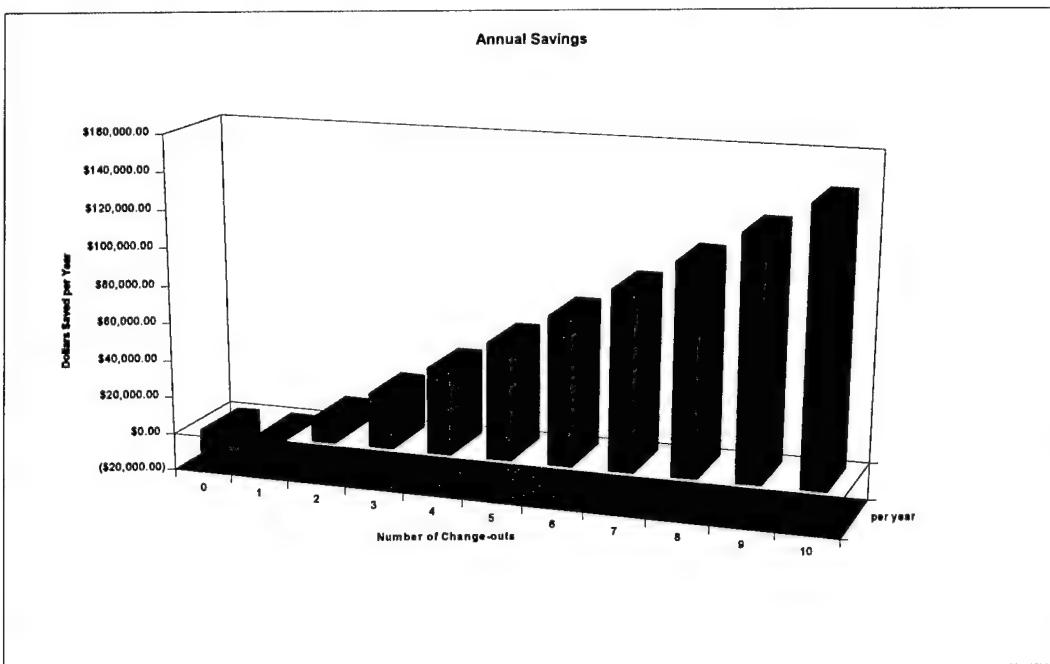


Figure 5: Annualized Cost Savings Based on WADR™ Usage

CONCLUSIONS

The WADR™ system as tested at the Watervliet Arsenal performed as expected. Acid concentrations were raised an average of 8% across the unit enabling the Arsenal to save over \$100,000 per year in reduced acid and waste costs. Economic analysis reveals that savings produced by the WADR™ system are tied proportionally with its use over a 10 year life span. In addition to the economic savings that can be realized, improved process control will also result. The current system of operation produces large swings in acid concentration. By utilizing the WADR™ system, acid concentrations can be maintained at near constant levels resulting in a well defined process that produces a more constant quality product. Another area of importance that is difficult to measure in dollar terms is the importance of reduced reagent and waste disposal in today's manufacturing arena. Permanent installation of the WADR™ system will enable the Watervliet Arsenal to operate a "green" process with respect to its acid disposal issues.

INNOVATIVE APPLICATIONS

**PLASMA TECHNOLOGY:
A TOOL FOR HAZARDOUS WASTE VITRIFICATION**

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ABSTRACT

A thermal plasma is an electrically conductive gas capable of generating temperatures up to 10000°C near its column. The energy generated by plasma arcs has been recently applied to hazardous waste control. The technology involves subjecting hazardous material to high temperatures with the purpose of immobilizing non-volatile chemical species into a non-leachable matrix. Plasma arc vitrification processing is well suited for special waste disposal requirements. In addition to its ability to sustain high temperatures, other attractive plasma technology features include its flexibility to operate in either an oxidizing or reducing environment, resultant waste volume reduction, low gas throughput, and flexibility to treat a large variety of waste types. Since 1989 the U.S. Army Corps of Engineers Construction Engineering Research Laboratories have been active participants in the research and developmental efforts undertaken to establish this technology as an efficient, economical, and safe hazardous waste immobilization tool. This paper will provide both a plasma arc technology overview and discuss Army/Department of Defense unique hazardous waste disposal needs, such as pyrotechnic smoke assemblies, thermal batteries, proximity fuzes, and contaminated soil which may be met through utilization of this tool. Specific examples of feasibility studies, Construction Productivity Advancement Research (CPAR) projects, and demonstrations undertaken to immobilize environmentally hazardous materials will be provided. Results of completed activities and on-going developments such as mobile plasma arc systems and dual torch demonstration plans will also be presented.

1. INTRODUCTION

Accumulating stockpiles, high storage costs, and the potential for long-term liability are illustrative examples defining the magnitude of the hazardous waste disposal issue facing both governmental and private organizations. The downsizing of the Department of Defense (DoD) presents governmental entities with the challenges of weapons disposal in addition to the necessity to be accountable for annual hazardous waste production. In a recent article highlighting the DoD's 1996 environmental goals, it was stated that the DoD operates 400 industries and disposes of 281 million pounds of hazardous waste annually¹. The DoD is subject to challenging and strict environmental program standards. One environmental requirement in the recently updated 'Environmental Measures of Merit' is the need for the DoD to reduce its hazardous waste disposal by half (based on a 1992 baseline) by calendar year 1999².

One of the technical challenges in disposing of hazardous wastes is the wide variability in waste media. Hazardous waste may either be solid or liquid waste streams or may contain such environmental hazards as asbestos, heavy metals, or organics or any combination of the mentioned waste components. The U.S. Environmental Protection Agency (EPA) has identified eight Toxicity Characteristic Leaching Procedure (TCLP)

metals which represent environmental hazards and whose disposal are strictly regulated. Figure 1 summarizes these metals and their prevalence in various military applications. In addition, in fiscal year 1994, the U.S. Army generated 640 tons of multi-phase toxic containerized liquids, 523 tons of bulk toxic pumpable liquids, 530 tons of multi-phase containerized solvents, and 128 tons of pumpable solvents³. Current treatment of these liquid containing waste streams cost approximately \$1250 to \$2700 per ton.

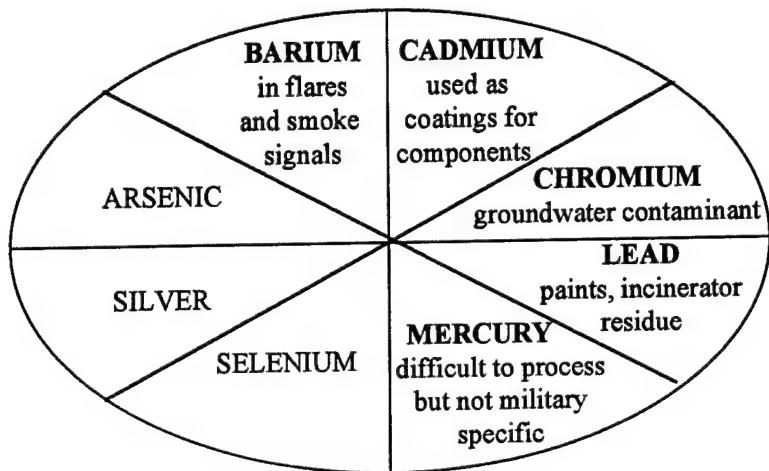


Figure 1. TCLP metals of interest to the military.

Various waste treatment/disposal methodologies have and continue to be evaluated for the environmental remediation of hazardous contaminated materials. Plasma arc technology has been identified as one safe and effective tool for the conversion of contaminated media into chemically inert solids no longer requiring disposal in EPA hazardous waste approved landfills. This paper will summarize the role that plasma arc technology plays in the disposal of DoD hazardous media.

2. THERMAL PLASMA ARC TECHNOLOGY

A plasma is an electrically conductive gas. Plasmas are generated when an electromagnetic force causes electrons to be pulled apart from atomic nuclei resulting in an ionized gas. In plasma arc technology, a torch is used to generate controllable plasma temperatures in the range from 1500°C to 7000°C. Several processing benefits associated with plasma technology include high thermal efficiency (resulting in fast reaction kinetics); flexibility in choice of process gas environment; substantial waste volume reduction; high energy density, thus adequacy in utilizing smaller processing reactors; no material pretreatment is required; and the need for less pollution abatement equipment due to the lower demand for air and absence of fossil fuels.

The strategy employed in plasma arc technology involves subjecting contaminated material to the high temperatures of the plasma and chemically combining the non-volatile components into a matrix material, such as soil, so that the processed material, upon solidification, represents an inert, chemically stable material. The resulting matrices will immobilize the hazardous components and prevent them from further contamination of the environment. A schematic overview of several of the various stages involved in thermally treating wastes using plasma technology is provided in figure 2.

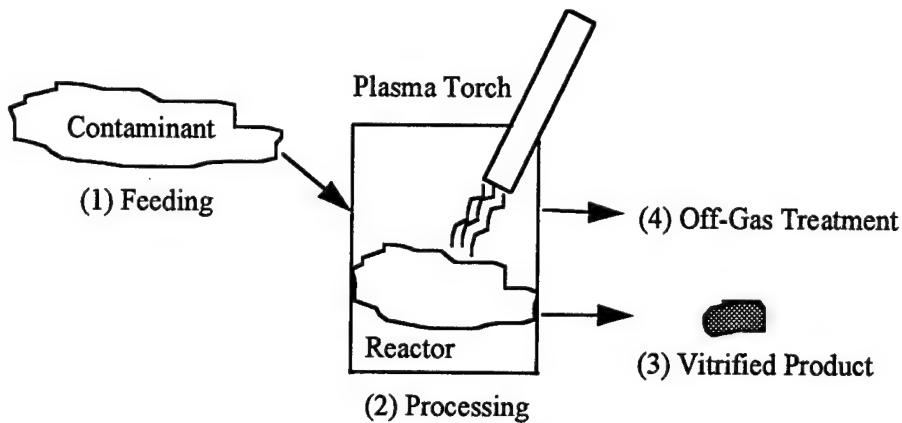


Figure 2. Schematic representation of plasma arc processing.

Introduction of the waste material into the furnace represents the initial challenge in plasma thermal treatment. Currently improvements are being made in regard to development of feeding mechanisms to minimize waste handling. Presently difficulties in designing "universal" feeding mechanisms exist due to the variability of the waste form. For instance, the wastes may be in the form of solid, liquids, large capacity drums, relatively fine particulate, etc., or any combination of the mentioned waste streams.

During the actual processing of the waste, a plasma torch is used to generate the high temperatures (typically several thousand degrees Centigrade) necessary to break the chemical bonds present in the waste material. The original components are then either melted down into elemental form (in the presence of a reducing atmosphere), oxidized into a variety of metal oxides, or a combination of the two, with the metals separating to the bottom of the melt container. The characteristics of the resulting vitrified product are a function of the torch gas/chamber environment, composition of the materials present within the plasma chamber, residence time of the waste during processing, and homogeneity of the treatment. Examples of suppliers of plasma torch systems in the United States include Plasma Energy Corporation (Raleigh, North Carolina), Retech, Incorporated (Ukiah, California), and Westinghouse (Pittsburgh, Pennsylvania).

The plasma treated melt is tapped or poured out of the processing chamber. Once cooled, the solidified mass, referred to as the slag, can be characterized as a vitrified, or glass-like rock. The potential of using this vitrified residue as various by-products such as aggregate, bricks, or gravel is possible. More importantly, once thermal plasma processed, the original hazardous waste now exists as a non-hazardous landfill waste. Various feasibility studies^{4,6} have indicated the consistency of slag products to pass toxicity characteristic leaching procedure and durability testing.

Highly volatile chemical species can escape out of the main reaction chamber before they are combined into the melt. Consequently, off-gas treatment systems are necessary to trap particulate and destroy any residual organics before they are released into the atmosphere. Plasma system design engineers are challenged with the need to develop off-gas treatment units which can meet the emissions controls requirements of thermal plasma processing yet keep the costs reasonable so that the vitrification process remains an economic feasibility. An overview of some of the most recent gaseous monitoring and emissions control methodologies used in plasma systems are included in the proceedings of a recent international symposium dedicated to environmental plasma processing applications⁷.

3. DOD RELATED PLASMA ACTIVITIES

The DoD generates wastes distinct from commercial industries because of its unique mission. The Army, for instance, generates such items as thermal batteries and proximity fuzes which have no equivalent in the civilian industry. Thermal plasma arc technology is capable of safely and efficiently destroying components or assemblies which contain such toxins as heavy metals and asbestos such that they can be disposed of safely in non-hazardous landfills and so that no "footprint" of the technology that went into the components can be identified.

Plasma arc technology has been a useful thermal treatment tool in the metallurgy and ceramics industry for a number of years. However, only since the middle to late 1980's has the technology been examined as a tool for hazardous waste destruction and immobilization. As indicated in figure 3, the research and developmental (R&D) efforts aimed at applying plasma arc technology toward waste remediation applications involves participants from various institutions. The following section describes some of the collaborative R&D efforts between various organizations, with particular attention being given to the U.S. Army and its sundry plasma technology environmental endeavors.

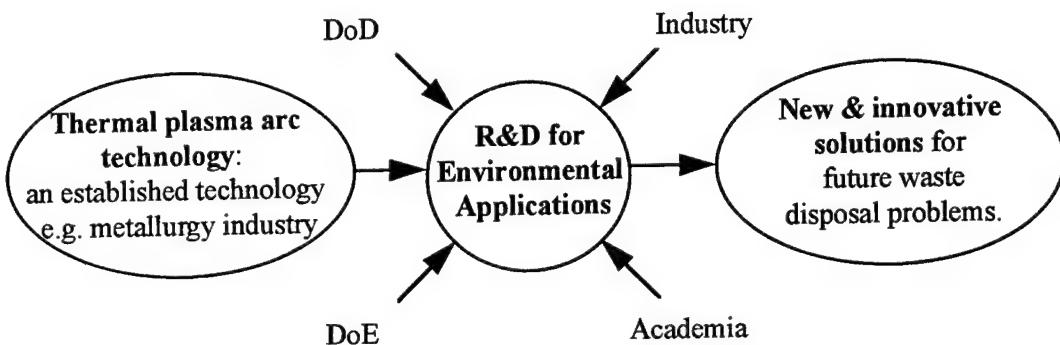


Figure 3. Plasma technology waste remediation players.

3.1 U.S. ARMY ACTIVITIES

3.1.1 Construction Productivity Advancement Research Project

Asbestos fibers and asbestos contaminated materials are tightly regulated as they are carcinogenic. Currently, asbestos removed from both public and private buildings must be deposited in Class I EPA regulated landfills. As landfill charges are volumetrically based, disposal of asbestos can be costly. With the possibility of reduced or prohibited use of Class I landfills, alternative means of dealing with asbestos contaminated materials are urgently needed.

Since 1989, the U.S. Army Corps of Engineers have supported a Construction Productivity Advancement Research Project (CPAR) utilizing plasma arc technology for the conversion of asbestos into harmless rock-like products. The CPAR project was conducted under the coordination of USACERL and the Georgia Institute of Technology using one of Plasma Energy Corporation's torch systems^{6,8}. The experimental results of the first stage of this two-phase program indicated that plasma arc technology provided successful immobilization of

chrysotile asbestos while meeting the standards for asbestos exposure. An economic analysis of the plasma processing of asbestos yielded positive indications for the success of a mobile plasma asbestos pyrolysis system (PAPS). It was concluded that a PAPS would be an economically competitive alternative to landfilling asbestos contaminated material. The attractiveness of the technology is apparent when the ever increasing costs for hazardous waste liability and transportation to appropriate landfill sites are considered.

The second phase of the asbestos CPAR project involved supporting the design of a PAPS asbestos treatment unit⁹. Research was conducted on asbestos contaminated items such as floor tile, roofing tile, and transite panels obtained from buildings in the Atlanta area. An economic analysis of a mobile trailer mounted 500 kW torch plasma system indicated that the cost of thermally treating the asbestos using plasma technology would be approximately \$200 per ton. These costs currently approximate the average asbestos treatment costs at Class I EPA approved landfills.

Further R&D work on on-site waste remediation is greatly needed to enhance the technology's capabilities. The significance of asbestos vitrification for the DoD is the reduction in abatement costs relating to asbestos transportation and disposal and the mitigation of a toxic material through conversion into an inert slag.

3.1.2 Applied Research and Development Activities through ME, Inc.

The Army has used the DoE contractor, MSE, Inc. (Butte, Montana) to perform various plasma processing runs of Army unique hazardous wastes and to conduct various R&D activities aimed at advancing plasma technology applied to environmental remediation issues. Both the Army Research Development and Engineering Center (ARDEC) and USACERL have and continue to employ the various plasma units at MSE for both applied research and technology advancing developments.

For example, MSE plasma processed proximity fuzes for ARDEC early in calendar year 1993. Processing results indicated that plasma technology was capable of safely and efficiently destroying the fuzes¹⁰. Presently MSE is conducting the necessary tests suitable for the thermal destruction and demilitarization of stockpiled ordnance¹¹. All of the feasibility examinations conducted for Army unique hazardous wastes have documentable challenges and lessons learned ranging from the initial waste feeding through processing to post-analytical product characterization. Some of these challenges include analytical ambiguities due to the presence of previously processed materials within the chamber, emissions concerns, particularly with regard to the generation of NO_x, and particulate formation and the loss of highly volatile organics and heavy metals. Work is continuing in these areas not only by MSE, but by other environmental plasma technology players.

MSE is participating in a technology advancement applied research activity, namely the development of a hybrid torch which can be independently or simultaneously operated in either a transferred or non-transferred arc mode. Both transferred arc torches and non-transferred arc torches have waste streams in which they are best suited for treating (see for example reference 12). By combining the two arc modes, plasma torch operation would be independent of the type of waste. The same torch could be used to treat either solid, liquid, or any combination sludge type waste. The final torch configuration has been selected from a number of proposals with the fabrication and testing of the dual torch in progress. This work is being conducted with the assistance of USACERL. One of the anticipated benefits of the hybrid torch is the reduced cost of processing multi-phase hazardous wastes.

Improvements in the logistics of operating a plasma furnace is a topic that has been studied by MSE with the support of the Army Corps of Engineers. Long term endurance tests have been conducted to pinpoint areas in which improvements in plasma systems could be made to increase the availability of the plasma processing units for environmental remediation efforts. In addition, process optimization studies have yielded observations and

recommendations on the following areas: feeding mechanisms improvements; slag quality control; mass balance accountability; and recommended improvements in gaseous emissions control. Design and implementation of a small scale plasma furnace have proven to be an effective tool for conducting preliminary or initial plasma runs under a more controlled environment with reduced operating costs.

3.1.3 Feasibility Studies at Ritech, Inc.

Ritech, Inc. (Ukiah, California) has participated in various plasma activities for the Army since 1992. Feasibility studies have been conducted on various military unique wastes. In addition to plasma treating soil contaminated with RCRA defined heavy metals and organic compounds, feasibility examinations of thermal batteries, incinerator ash, pyrotechnic smoke assemblies⁵, and sludge¹³, have been conducted using Ritech's Plasma Centrifugal Furnace (PCF 1.5) and Small Scale PACT unit. In general, those items containing heavy metals were found to pass TCLP tests while organic destruction was successfully achieved through thermal plasma processing.

Presently, the National Defense Center for Environmental Excellence (NDCEE) is evaluating the use of plasma arc technology for treatment of complex military wastes as initially requested by the U.S. Army. The initial phase of this evaluation involved plasma treating agricultural blast media, glass blast media, medical ash, and plastic blast media¹⁴. As summarized in an update of the NDCEE¹⁴, post-phase I testing included consideration of phase II testing waste streams by the representatives of the Tri-Services, NDCEE, and industry. Selection criteria for phase II testing included consideration of current waste treatment cost, DoD waste stream priority level, treatment difficulty level, waste availability for testing, and waste generation rate. One end product of this evaluation will be a report documenting recommendations to the DoD for designing, building, permitting, and installing full-scale plasma waste treatment facilities.

3.2 U.S. NAVY ACTIVITIES

Two of the major plasma related activities being coordinated by the U.S. Navy include an Advanced Technology Demonstration (ATD) and an Environmental Security Technology Certification Program (ESTCP). The goal of the ATD is to build a land-based prototype plasma treatment unit subject to specific technical requirements unique to Navy wastes.

In July 1995, ESTCP funding was provided to the U.S. Naval Research Laboratory and the Norfolk Naval Base (Norfolk, Virginia) to establish a plasma treatment unit to destroy dockside waste. Sartwell¹⁵ summarized the various logistical, regulatory, and technical challenges facing the designers and engineers of plasma units capable of destroying mixed solid and liquid hazardous waste. Ritech, Inc.'s plasma arc centrifugal treatment (PACT) unit systems have been chosen to support the technical requirements of the program.

3.3 U.S. AIR FORCE ACTIVITIES

The U.S. Air Force is developing the potential of plasma arc technology for the stabilization and destruction of bare base waste applications¹⁶. The Georgia Institute of Technology has recently been funded by the Air Force to develop a full scale technology demonstration for treatment of bare base waste such as domestic and hazardous and medical wastes. Work for this project is being conducted under the coordination of Tyndall Air Force Base.

4. SUMMARY

Plasma arc technology is a thermal treatment tool capable of safely and efficiently processing materials containing a large variety of environmental hazards such as heavy metals and asbestos. Utilization of this

technology allows waste candidates to be disposed of safely in non-hazardous landfills; and cost effectively when other waste treatment alternatives fail. Plasma arc technology is undergoing continuous development to improve system reliability and versatility. Research continues in the areas of torch life performance, specifically in the development of longer-life electrodes, while continued development in effluent stream minimization is ongoing to increase technology public and regulatory acceptance. The extensive use of this technology by DoD organizations within the Army and Navy illustrate the potential and feasibility of the technology to meet the ever growing waste disposal needs of an environmentally conscious world community.

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**Phytoremediation of Explosives-Contaminated Groundwater
In Constructed Wetlands:
II - Flow Through Study**

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ABBREVIATIONS

2A-DNT	-2-Aminodinitrotoluene
4A-DNT	-4-Aminodinitrotoluene
CO ₂	-Carbon Dioxide
°C	-Degrees Centigrade
cm	-Centimeters
cm ²	-Centimeters square
COD	-Chemical Oxygen Demand
D O	-Dissolved Oxygen
DoD	-Department of Defense
g/l	-Grams per liter
g/cm ²	-Grams per centimeter square
g/m ²	-Grams per meter square
mg/l	-Milligrams per liter
NPDES	-National Pollutant Discharge Elimination System
HMX	-Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HPLC	-High Performance Liquid Chromatography
I.U.	-International Units
mL/min	-Milliliter per minute
MIRP	-Military Interdepartmental Purchase Request
MRS	-Milk replacement starter
N	-Nitrogen
ORP	-Redox potential
P	-Phosphorus
ppb	-Parts per billion
RDX	-Hexahydro-1,3,5-trinitro-1,3,5-triazine
TNB	-Trinitrobenzene
TNT	-2,4,6 Trinitrotoluene
TVA	-Tennessee Valley Authority
U.S.	-United States
USAEC	-United States Army Environmental Center

SECTION 1.0

INTRODUCTION

This study is a follow-up to a batch study (Study I), which was undertaken to evaluate the utility of constructed wetlands, both surface and subsurface flow, for remediating explosives contaminated groundwater. The present study, (Study II), a 30 day microcosm study was conducted for the Army Environmental Center as part of a continuing technology demonstration program. Objectives of Study II included validating findings of Study I and evaluating an expanded range of experimental wetland environments in flow-through system mode with respect to their abilities to remediate contaminated groundwater containing low concentration of TNT, RDX, HMX, and TNB.

SECTION 2.0

MATERIALS AND METHODS

Twenty microcosms were used in this study, each of which consisted of an opaque glass aquaria (38 liters) partitioned with glass into either 4 or 2 cells (see Figures 2-1a and b respectively). They were located within a large research greenhouse at TVA's Constructed Wetlands R&D Center. The experimental design was completely randomized in factorial arrangement to test three main factors at two levels. Main factors and their respective levels were:

- Wetland species (parrot feather *Myriophyllum aquaticum* vs. canary grass, *Phalaris arundinacea*);
- Initial planting density (25 g/l versus 50 g/l on a wet weight basis);
- Level of fertility (350 mg/l versus 700 mg/l milk replacement starter).

Table 2-1 summarizes treatment designation and treatment factors. The experimental design, in factorial arrangement, included three factors, each at two levels for the subsurface flow design. The surface flow (lagoon system) evaluated fertility rate and plant density, but only for the plant species parrot feather. Treatment designations followed the convention as follows:

- The first letter refers to the species designation (C = canary grass, P = Parrot feather);
- The second letter refers to the planting density (L = low, H = high);
- The third letter refers to the fertility level (L = low, H = high).

Systems designation are in parenthesis following treatment designations and are as follows:

(W) = wetlands, subsurface flow; and (L) = lagoon, surface flow.

Plants were apportioned to microcosm cells on a unit area basis (g/cm^2), such that all cells within a treatment had similar biomass per unit area. Canary grass and parrot feather were planted in the

Table 2-1
Treatment Designations and Summary of Treatments.

TREATMENT DESIGNATION	REPS. (1)	MICROCOSM (type)	CELLS ¹ (submicrocosm)	SPECIES ²	DENSITY (g/microcosm)	FERTILITY LEVEL (mg/L)
PLL (W)	2	WETLAND ²	4	P. FEATHER	300	350
PHL (W)	2	WETLAND	4	P. FEATHER	600	350
PLH (W)	2	WETLAND	4	P. FEATHER	300	700
PHH (W)	2	WETLAND	4	P. FEATHER	600	700
CLL (W)	2	WETLAND	4	CAN. GRASS	300	350
CHL (W)	2	WETLAND	4	CAN. GRASS	600	350
CLH (W)	2	WETLAND	4	CAN. GRASS	300	700
CHH (W)	2	WETLAND	4	CAN. GRASS	600	700
PLL (L)	1	LAGOON	2	P. FEATHER	300	350
PHL (L)	1	LAGOON	2	P. FEATHER	600	350
PLH (L)	1	LAGOON	2	P. FEATHER	300	700
PHH (L)	1	LAGOON	2	P. FEATHER	600	700

⁺

¹ Cells A and B in rock filters maintained anaerobic, cells C and D maintained aerobic via air-lifts (recurrent reciprocation at two hour intervals).

² Wetlands operated as subsurface flow with terminal reciprocating cells.

³ Parrot feather (*Myriophyllum aquaticum* = *braziliense*); canary grass (*Phalaris arundinacea*).

FIGURE 1A. SUBSURFACE-FLOW WETLAND MICROCOISM (W)

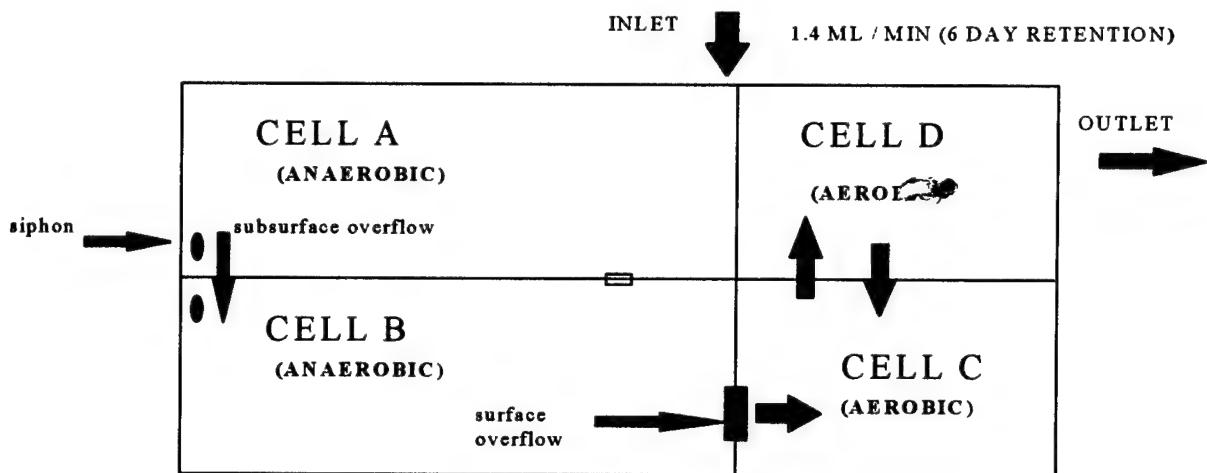
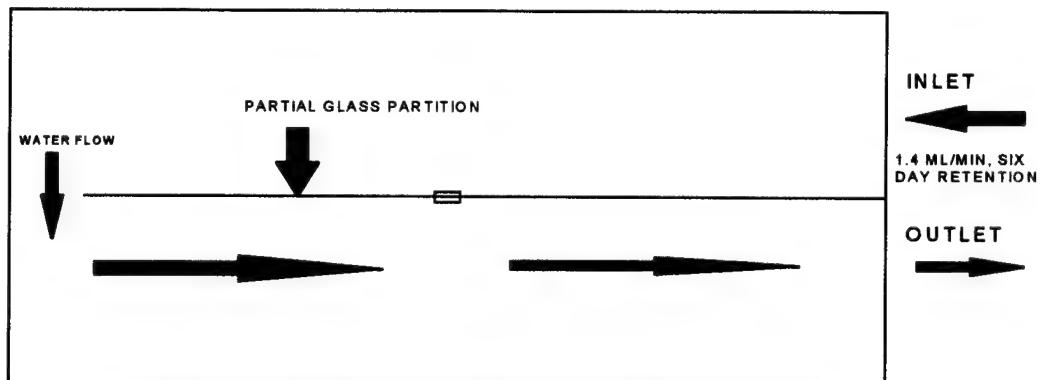


FIGURE 1B. SURFACE-FLOW LAGOON MICROCOISM (L)



Figures 2.1 A and B
Plan view of wetland (W) and lagoon (L) microcosms
illustrating cell partitions, flow rates, and water treatment flow-paths.

rock based wetlands (W), such that the crown was above the water level. In the lagoon systems (L), parrot feather was placed into the shallow water and distributed to ensure even surface coverage. On a dry matter basis the high and low biomass treatments were planted at densities equivalent to 899 and 449 g/m² (canary grass) and 971 and 485 g/m² (parrot feather), respectively. Microcosms were planted, fertilized, and operated under experimental conditions for 15 days prior to experimentation to allow plants and microbial populations to become established and acclimatized.

Initial water volume in all treatments was equal to 12 liters. Contaminated groundwater used in this study was pumped from Milan well MI 146 (Milan Army Ammunition Plant, Milan, Tennessee), transported to TVA and stored on site in large stainless steel tanks until used in experiments. Average concentrations of explosives (mg/l), as measured in the storage containers were as follows: TNT, 2.153; RDX, 2.732; HMX, 0.160; and TNB, 0.154.

Flow rate of contaminated water to each microcosm was maintained at approximately 1.4 ml/min with peristaltic pumps, for a calculated hydraulic retention time of 6 days. This retention time was selected based on an earlier study that was designed to evaluate explosives remediation in batch loaded (static non-flow-through), rock biofilters and shallow planted lagoons (see Batch Study I).

The four cell aquaria, simulating subsurface-flow wetlands (W), were back-filled with bacteria-laden river gravel (void space = 35-40 %) to a depth of approximately 22 cm. Gravel was collected from an outdoor anaerobic subsurface flow wetland which had been in operation for over 1 year, transported to the greenhouse and placed into microcosms. Care was taken to maintain the "harvested" rocks under anaerobic conditions so that the anaerobes were not exposed to aerobic conditions.

Figure 2-1a illustrates a plan view of the wetland microcosms detailing flow paths and position of inlet, subsurface siphon and outlet. Cells A and B of each wetland microcosm (W), each had surface areas equal to 416 cm² and were designed to maintain anaerobic conditions (no aeration); cells C and D each had surface areas equal to 214.5 cm² and were designed to remain aerobic.

Cells C and D of wetland microcosms were aerated using paired air lifts which were operated sequentially at two hour intervals; this process of sequential and recurrent aeration is referred to as reciprocation. For example, during reciprocation cycle one, water in each C cell was air-lifted to and stored in the contiguous D cell. Water in excess of cell D's freeboard was allowed to leave the system via an external standpipe. The process was reversed every two hours. The process of air-lifting water facilitated mild aeration and as water was removed from the pumped cell, the rock backfill material, plant roots, and fixed-film microbial populations were exposed to atmospheric oxygen for approximately two hours. Sequential anaerobic-aerobic environments have been found to be useful in remediating recalcitrant compounds and their byproducts, and to facilitate removal of excess carbon and nutrients which are often used to fertilize microbial/plant remediation ecosystems.

The 2-cell aquaria (Figure 2-1 b), simulating shallow lagoons (L), were designated as "controls" (no rock substrate, no aeration) and were stocked with parrot feather *Myriophyllum aquaticum*, either at 25 g/l or 50 g/l. Two fertility treatments were also imposed on each plant stocking density (350 versus 700 mg/l fertility, milk replacement starter). These non-replicated treatments were not a part of the factorial experiment, but were included to allow comparisons between rock-based wetlands and lagoon systems.

Organic fertilizer consisting of a commercial grade of milk replacement starter (MRS), was used as the sole source of exogenous carbon and macro / micro-nutrients (Table 2-2). At the initiation of the experiment, time = 0, contaminated water was batch fertilized with MRS. Twelve liters of the fertilized munitions-contaminated water mixture was apportioned to each microcosm. Subsequently, unfertilized contaminated groundwater was pumped via peristaltic pumps at a rate of 1.4 ml/min into the inlet of each microcosm. Based on void space, water volume, and flow rate this was equivalent to a six day retention time; two days in each of cells A and B and one day in each of cells C and D. With respect to the shallow lagoons (L), the six-day retention time was equally divided between cells A and B. On day 20 of the experiment, following collection of water samples, all microcosms were refertilized with a concentrated slurry of MRS equivalent to 4.2 or 8.4 grams of the powder. These rates of fertilization were based on the initial fertilization rates, i.e. 350 and 700 mg/l. The concentrated slurry was injected with syringes into each microcosm near the inlet (below the surface), to simulate a plug-flow situation. Subsequent sampling of TNT,

Table 2-2
Proximate Composition of Milk Replacement Starter Used as Organic Fertilizer in
TNT MICROCOsm STUDY II.

Crude protein, not less than	22.0%
Crude fat, not less than	20.0%
Crude fiber, not more than	0.5%
Calcium (Ca), not less than	0.75%
Calcium (Ca), not less than	1.25%
Phosphorus (P), not less than	0.70%
Vitamin A, not less than	20,000 I.U./lb
Vitamin D3, not less than	5000 I.U./lb.
Vitamin E, not less than	100 I.U./lb.
INGREDIENTS:	Dried whey, dried whey protein concentrate, dried whey product, dried skim milk, dried milk protein, protein modified soy flour, animal fat (preserved with ethoxyquin), lecithin, dicalcium phosphate, calcium carbonate, vitamin A acetate, D-activated animal sterol (source of vitamin D-3, vitamin E supplement, thiamine mononitrate, pyridoxine hydrochloride, folic acid, vitamin B-12 supplement, choline chloride, sodium silico aluminate, manganese sulfate, zinc sulfate, ferrous sulfate, copper sulfate, cobalt sulfate, ethylenediamine dihydriodide and sodium selenite. oxytetracycline (125 g per ton), neomycin base (250 g per ton).

RDX, HMX and byproduct compounds were sampled on day 6, 10, 20, and 30. Analysis of munitions and by-products was via HPLC. On each sampling date, 20-50 ml samples were collected from the 4-cell microcosms at the:

- Inlet,
- Overflow of cell A (siphon location),
- Adjacent to overflow of cell B, and
- Outflow of cell D.

In the two-cell microcosms, 20 ml samples were taken at the inlet, and at points in the flow path to approximate 2, 4, and 6-day retention. Samples collected for explosives determinations were stored and frozen in amber glass vials until analyzed. Analyses were conducted using HPLC.

Water samples were also sampled on a routine basis for COD (Hach Method), dissolved oxygen (D.O.), pH, conductivity and temperature using a water quality sonde (Yellow Springs Instruments, Yellow springs, Ohio). Redox potential (ORP), was measured via insitu probes (platinum electrode and calomel reference electrode) located near the inlet and outlet of each microcosm. Measurement of ORP was conducted at regular intervals to monitor changes in ORP as a function of treatment and location within the microcosms.

After 45 days of culture (15 days acclimation and 30 days of experiment), plant biomass was harvested from each microcosm, dissected into root and shoot portions (canary grass), or root, subsurface stem, and aerial shoot portions (parrot feather), allowed to "drip-dry", and weighed to the nearest 0.1 gram. Subsequently, the samples were placed into tarred paper bags and dried for 48 hours in a forced-air oven operated at 60 degrees centigrade. Oven-dried samples were reweighted to the nearest 0.1g and yields and standing crops were calculated on a g/m² basis.

For the purpose of this report, data has been compiled, averaged, and summarized in either table or graphical format. Simple correlation was used to demonstrate the relationship between redox potential and remediation of RDX.

SECTION 3.0

RESULTS AND DISCUSSION

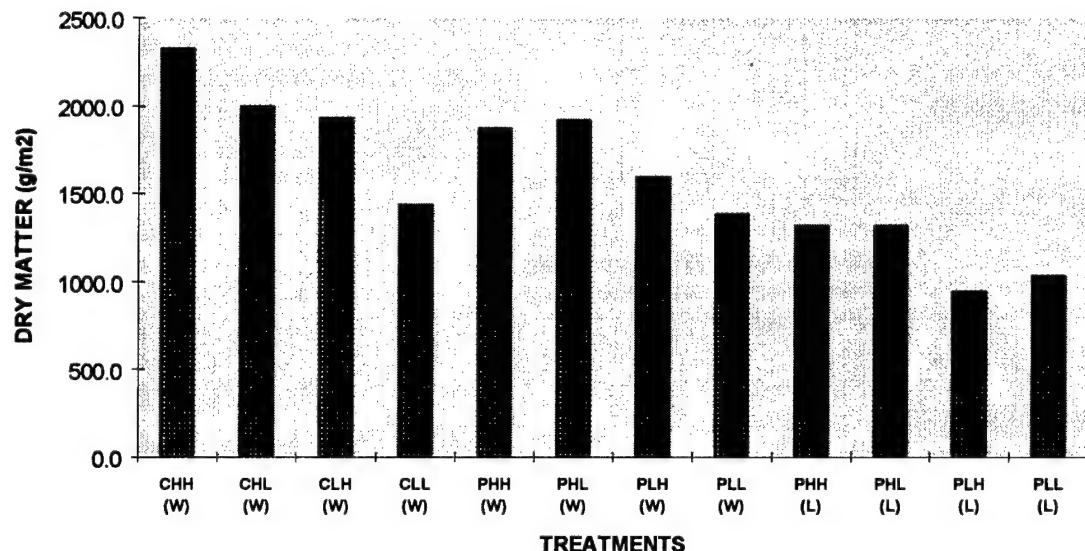
3.1 Plant Productivity, Growth, and Treatment Implications

Gross biomass of whole plants (roots, shoots and stems) expressed as g/m² dry matter, ranged from 881 to 2260 g/m². In wetlands treatments (W), canary grass responded in an additive manner to both increased density and fertility and under high density-high fertility conditions yielded 2203 g/m². In contrast, parrot feather tended to have higher yields (2262 g/m²), in the low fertility-high density treatment. In the lagoon systems (L), parrot feather yields were not additive, indicating possible yield by treatment interactions. Parrot feather production (gross), in the lagoon treatments were relatively low (825 to 1237 g/m²) except in the high density / high fertility treatment (20 81 g/m²).

Figure 3-1 illustrates gross production on a dry matter basis (initial biomass plus net production) as a function of treatment. Bottom bars, colored in blue, represent initial biomass at time of planting; while the top bars, colored in black, represent net production or yield. Notice that canary grass production responded to increases in fertility, but very little to increases in density. Parrot feather yields in the wetland systems also showed a strong response to fertilization at the low density, but a negative response to fertilization at the high density. These responses both indicate that at the high density, plant biomass may have been near carrying capacity. Parrot feather yields in the lagoon systems were significantly less than yields in the wetland systems, irrespective of fertility or plant density (Figure 3-1). Yields (g dry matter/m²), averaged over levels of fertility and density for canary grass and parrot feather were: canary grass (1244), parrot feather (wetlands, 958; and lagoons, 421).

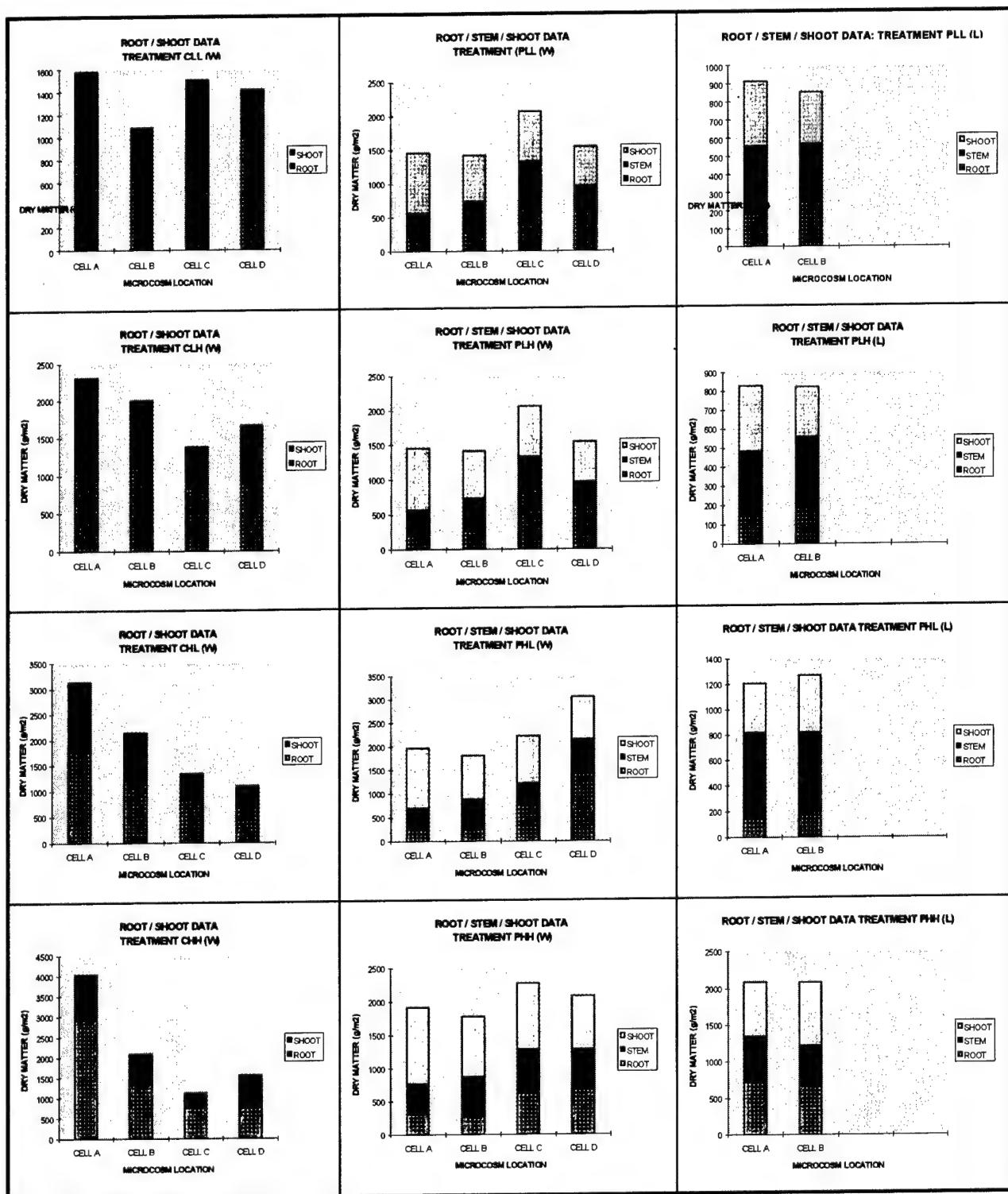
Closer examination of plant production data as a function of location (Cells A, B, C, D) and tissue type (root, sub-surface stem, and aerial shoot), reveals significant differences in species responses to density, fertility, and treatment system (Figure 3-2). Values are based on gross biomass production over a 45 day period during September and October, 1995 (15 day acclimation period and 30 day study).

PLANT PRODUCTIVITY



Initial planting density represented by upper bars, net production by lower bars, and gross production by sum of grass. Plant type are designated by the first letter of the treatment designation. The letter C designates canary grass; P designates parrot feather. Values represent production over a 45 day period (September - October 1995).

Figure 3-1
Initial Planting Density, Net Production, and Gross Production
for Canary Grass and Parrot Feather as a Function of Treatment.



Note: Y-axes have not been standardized across treatments).

Figure 3-2
Mean dry matter production of roots, stems, and shoots as a function of location, plant species, plant density, level of fertility, and treatment system.

Canary grass yields tended to decrease from cell-A to cell-D mostly as a result of nutrient limitations. Also, shoot biomass tended to decrease relative to root biomass (root/shoot ratios), as fertility and density increased. In contrast, parrot feather yields in similar wetland environments (W), tended to increase from cell A to cell D irrespective of fertility and density inputs. Also, the root to shoot ratio of parrot feather increased dramatically in the aerobic portions of the wetlands (cells C and D contrast cells A and B, Figure 3-2). Plant yield data and tissue growth partitioning are potentially important with respect to sustainability and treatment efficacy of the proposed treatment system(s). In start up operations, it will be necessary to augment with organic fertilizers to promote anaerobic conditions. However, over time the carbon fixed in the plants (plant tissue contains approximately 50% carbon on a dry matter basis), should become available to the microbial populations as the plants grow, senesce, and die. Plant leaf litter and dead roots and their attendant high oxygen demands will also decrease the impact of atmospheric diffusion of oxygen into the treatment wetlands.

With respect to plant growth patterns and tissue partitioning, it may be important to have planting schemes and treatment environments that promote high root to shoot ratios. Roots provide tremendous surface area for both microbial attachment and for direct uptake of nutrients, explosives and explosives by-products. Plant production data in this study would support planting canary grass near the inlet (strong response to high fertility) and parrot feather in the distal areas of the wetlands, including the reciprocating cells, (high root to shoot ratios at low fertility and in aerated environments).

3.2 Water Quality

Water quality parameters were averaged by treatment over sample dates ($n = 15$) for the 30 day trial. Means and standard deviations are summarized by in Table 3-1. Neither temperature nor pH values differed significantly among treatments and were relatively stable throughout the study. Notable differences in pH between A and D locations within the wetland systems were assumed to be due to reciprocation, subsequent off-gassing of CO_2 and a shift in the carbonic acid buffer system.

TREATMENT DESIGNATION	TEMPERATURE (°C)	ELECTRICAL CONDUCTIVITY (mS/cm)	DISSOLVED OXYGEN (mg/l)	pH (moisture)	REDOX POTENTIAL (mV) ¹
LOCATION	A ²	D ²	A ²	D ²	A ²
CLL (W)	22.5	21.5	185.3	222.9	5.6
	(3.7)	(3.5)	(33.4)	(42.5)	(1.7)
				(1.0)	(0.3)
CHL (W)	22.0	20.8	224.4	266.8	5.3
	(3.6)	(3.5)	(55.3)	(41.9)	(2.1)
				(1.6)	(0.2)
CLH (W)	22.0	20.9	239.0	276.7	5.0
	(3.6)	(3.5)	(69.1)	(59.3)	(2.4)
				(0.5)	(0.2)
CHH (W)	22.3	21.1	216.1	270.7	4.2
	(3.6)	(3.5)	(83.9)	(60.6)	(2.2)
				(0.5)	(0.2)
PLL (W)	22.3	21.3	156.7	188.6	5.2
	(3.8)	(3.6)	(45.3)	(41.1)	(1.3)
				(2.1)	(0.2)
PHL (W)	22.2	21.1	173.5	176.9	0.8
	(3.9)	(3.6)	(55.3)	(38.9)	(0.5)
				(1.9)	(0.2)
PLH (W)	22.0	21.0	208.4	219.5	1.1
	(3.9)	(3.7)	(71.3)	(66.5)	(1.3)
				(2.0)	(0.3)
PHH (W)	22.2	21.2	228.4	241.0	0.9
	(3.9)	(3.6)	(90.4)	(75.0)	(0.7)
				(2.5)	(0.2)
PLL (L)	22.3	21.8	67.7	45.8	5.5
	(3.7)	(3.6)	(40.0)	(37.6)	(2.7)
				(3.1)	(0.4)
PHL (L)	22.5	21.9	69.3	44.7	5.3
	(3.8)	(3.7)	(39.1)	(35.1)	(2.7)
				(2.8)	(0.4)
PLH (L)	22.3	21.9	96.9	80.1	3.0
	(3.8)	(3.7)	(50.0)	(57.5)	(1.6)
				(2.9)	(0.4)
PHH (L)	22.5	21.9	109.5	87.2	3.5
	(3.9)	(3.9)	(56.1)	(51.9)	(2.2)
				(2.1)	(0.3)
				(0.4)	(0.4)
				(75.6)	(68.4)

1. Redox values are uncorrected. Add 255 for corrected values.
2. Location A was proximate to the inlet, while location D was near the outlet of each microcosm, irrespective of system

Table 3-1
Water Quality Parameters: Means and Standard Deviations, (+/- 1 stddev) as Monitored During the 30 Day Trial (September / October 1995).

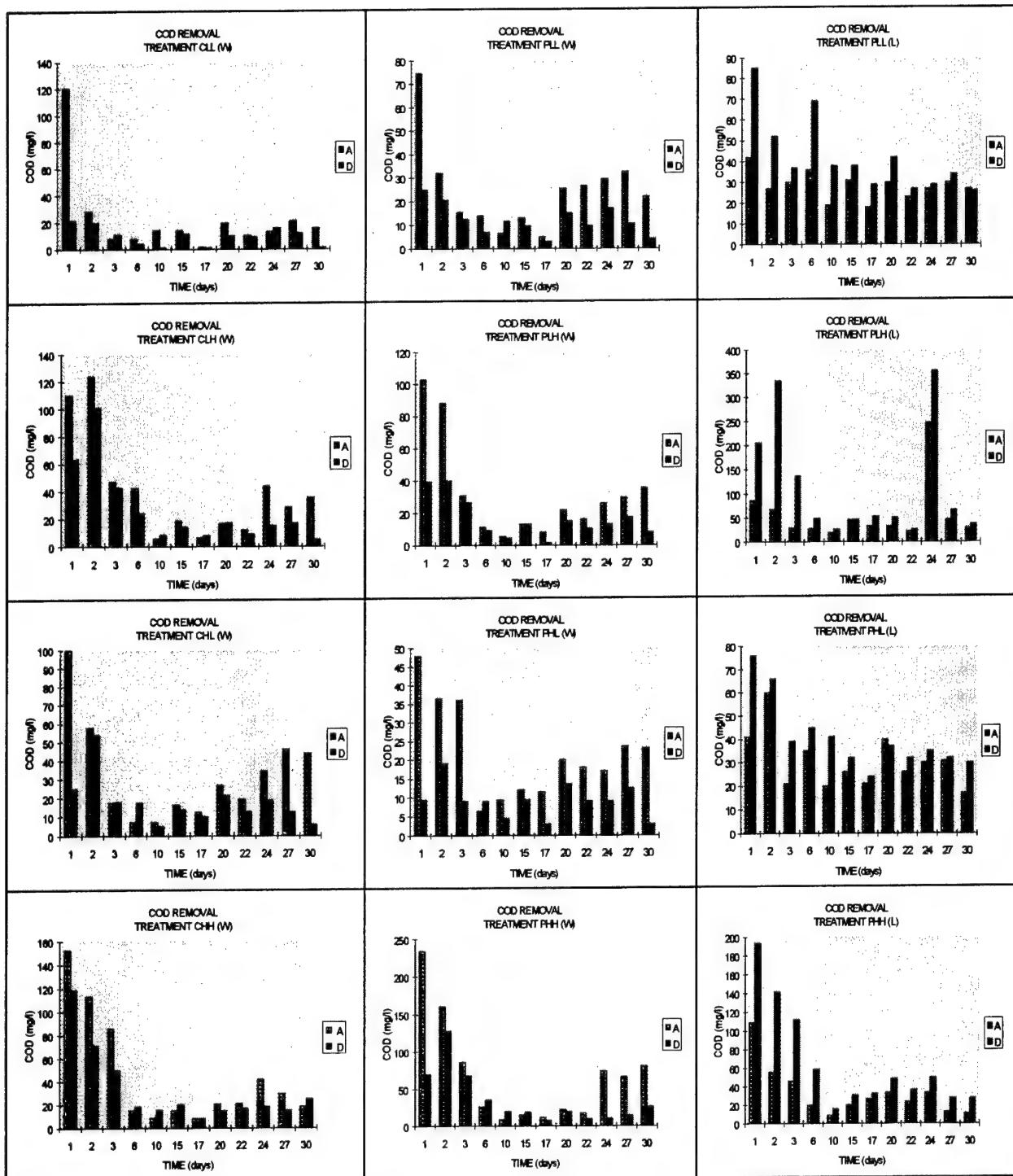
Electrical conductivity, as measured by specific conductance, did vary among treatments and locations within treatments. Treatments with a rock backfill had mean values ranging from 172 to 278, while lagoon treatments had values ranging from 46 to 110. These differences were due to three factors:

- Dissolution of minerals from the rocks in the wetland treatments,
- Differences in levels of fertility,
- Rapid uptake of minerals by parrot feather in the lagoon treatments, and subsequent transport of the minerals to the leaf surface.

A white powdery mineral salt accumulated on the parrot feather leaves. Salt accumulation was probably magnified because of the greenhouse environment (no rain to rinse mineral salts from leaves).

Dissolved oxygen concentrations (D.O.), and redox potentials differed among treatments (Table 3-1), and were influenced by treatment type (lagoon versus wetland), level of fertility and plant species and biomass. In general, D.O. concentrations and redox values were significantly lower in wetland treatment cells (A and B), with rock backfill than in shallow lagoon treatments. These differences can be explained due to differences in community respiration rates which influence carbon metabolism, D.O. concentrations and oxidation-reduction potential. The rock substrate in the subsurface flow wetlands provided considerable surface area for fixed-film microbial populations and their attendant high respiration rates. Also, lagoons systems have more surface area in contact with the overlying atmosphere, and thus reoxygenation rates due to diffusion were greater in those treatments. Furthermore, dissolved oxygen derived from photosynthesis was greater in the lagoons since much of the parrot feather biomass was under the surface of the water.

Chemical oxygen demand (COD) is used as a measure of the oxygen equivalent of the organic matter content of a sample, and can be used to track the degradation of labile organic compounds, such as milk replacement starter. In lagoon environments it can also be used to track the endogenous formation of new dissolved organic compounds (net productivity), such as photosynthates or plant root exudates. Figure 3-3 illustrates COD dynamics as a function of



Notes: 1). Cells were fertilized with milk replacement starter on days 0 and day 20 (see text for rates and methods).
 2). Y-axes are not standardized across treatments.

Figure 3-3
COD Removal Rates as a Function of Treatment, Location (Cell),
and Days Post-Fertilization

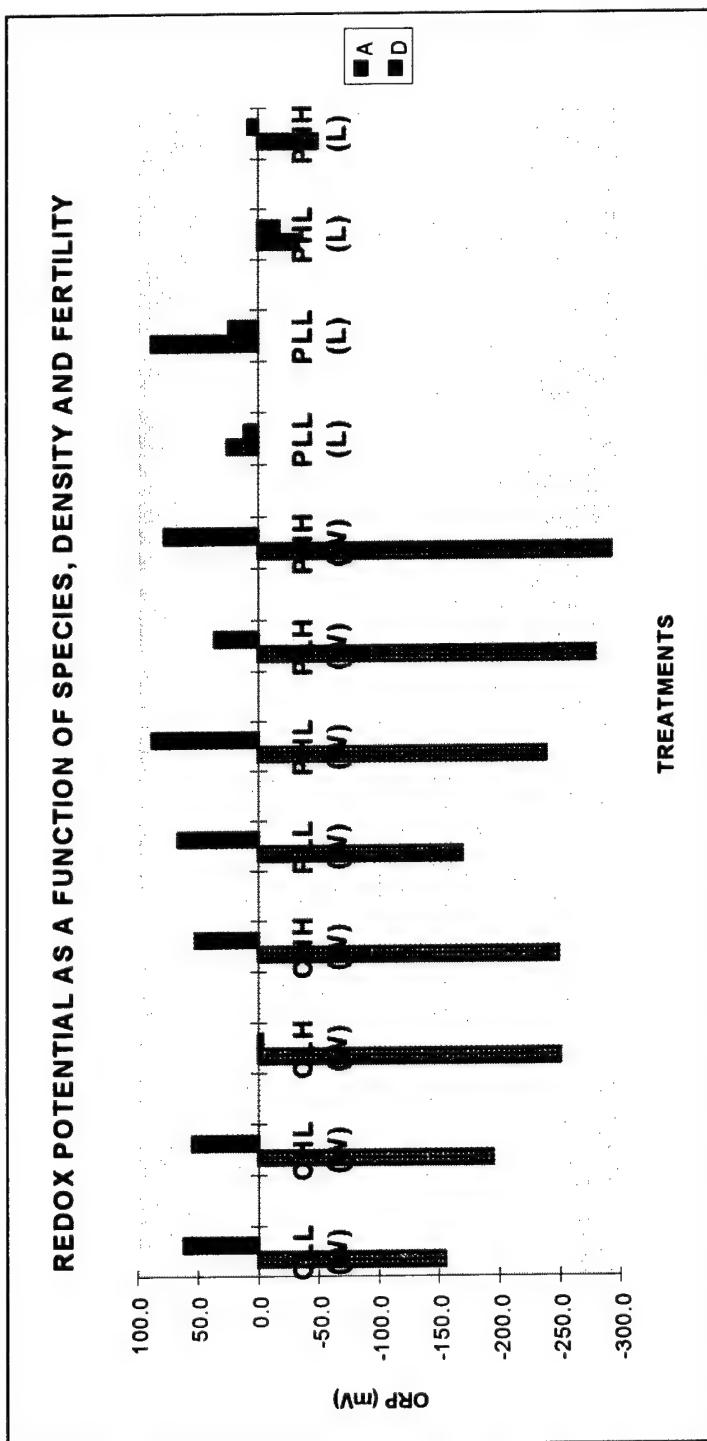
treatment, time and location. Three important aspects of this graph should be noted:

- The relatively rapid decline in COD within the first six days in wetland treatments versus lagoon treatments,
- The relative difference in COD values among locations (A versus D) within wetland treatments,
- And the small but perceptible increase in COD between location A and B within the lagoon treatments.

The increase in COD is an indication that parrots feather in lagoon environments is “leaking” organic matter back into the water in excess of the systems ability to oxidize the organic matter. Under extreme conditions, this could be considered pollution, as it has an inherent biological oxygen demand that may violate NPDES permit limits.

Redox potential plays an important role in explosives bioremediation technologies. Establishing a wide range of redox zones within the treatment train allows for a diversity of microbial populations which can effectively oxidize and/or reduce munitions, their by-products and organics. Figure 3-4 compares average redox potentials of the various treatments with respect to location (near inlet A versus near outlet D). The figure illustrates the relative contribution of plant species, plant density and fertility to negative redox values (see stair step pattern of negative values). Also, the figure vividly illustrates the differences in performance between subsurface-flow wetlands (W) and surface-flow lagoons (L). At low fertility, average redox values for the lagoon systems were positive in both cells A and B. At high fertility, the lagoon systems exhibited average values that were slightly negative, but still significantly less negative than comparable wetland cells.

Figures 3-5, 3-6, 3-7, illustrate changes in redox values for each treatment over time. Systems were fertilized in batch mode (completely mixed) on day 0 and again on day 20; however on day 20 the fertilization was performed by injecting a concentrated solution of MRS near the inlet of the system. Graphs have been grouped to facilitate comparison of canary grass and parrot feather under common fertility /density treatments. Figures 3-4, 3-5, 3-7, and 3-7 illustrate



Means are based on 12 observations over a 30 day period (September-October, 1995). Blue bars represent values in cell A and brown bars represent values in cell D (for wetland systems) and cell B for lagoon systems.

Figure 3-4 Average redox values as a function of treatment, location, and system (wetland versus lagoon).

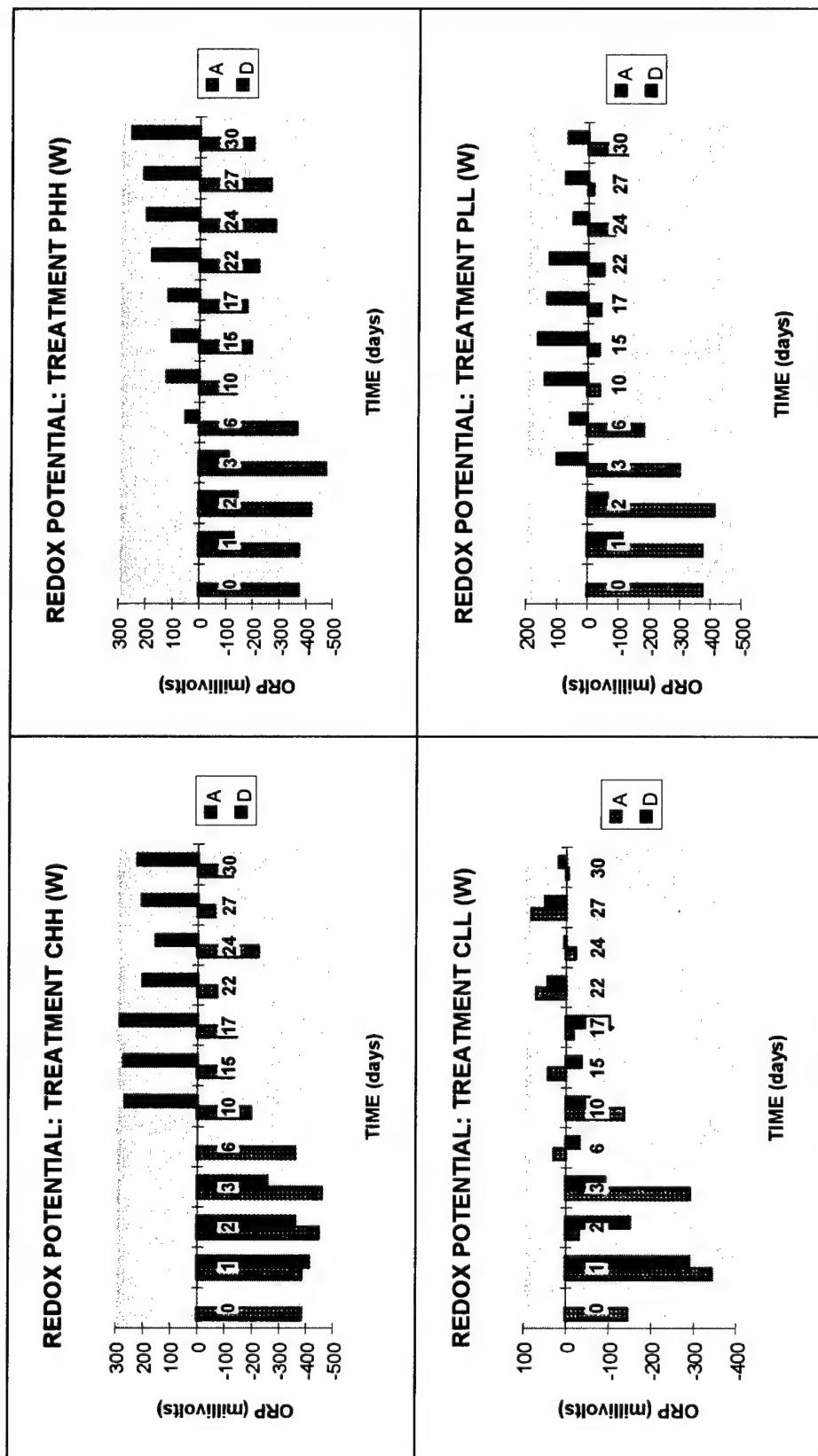


Figure 3-5

Redox potential as a function of wetland treatments and time for: CHH(W), CLL(W), PHH(W), and PLL(W)

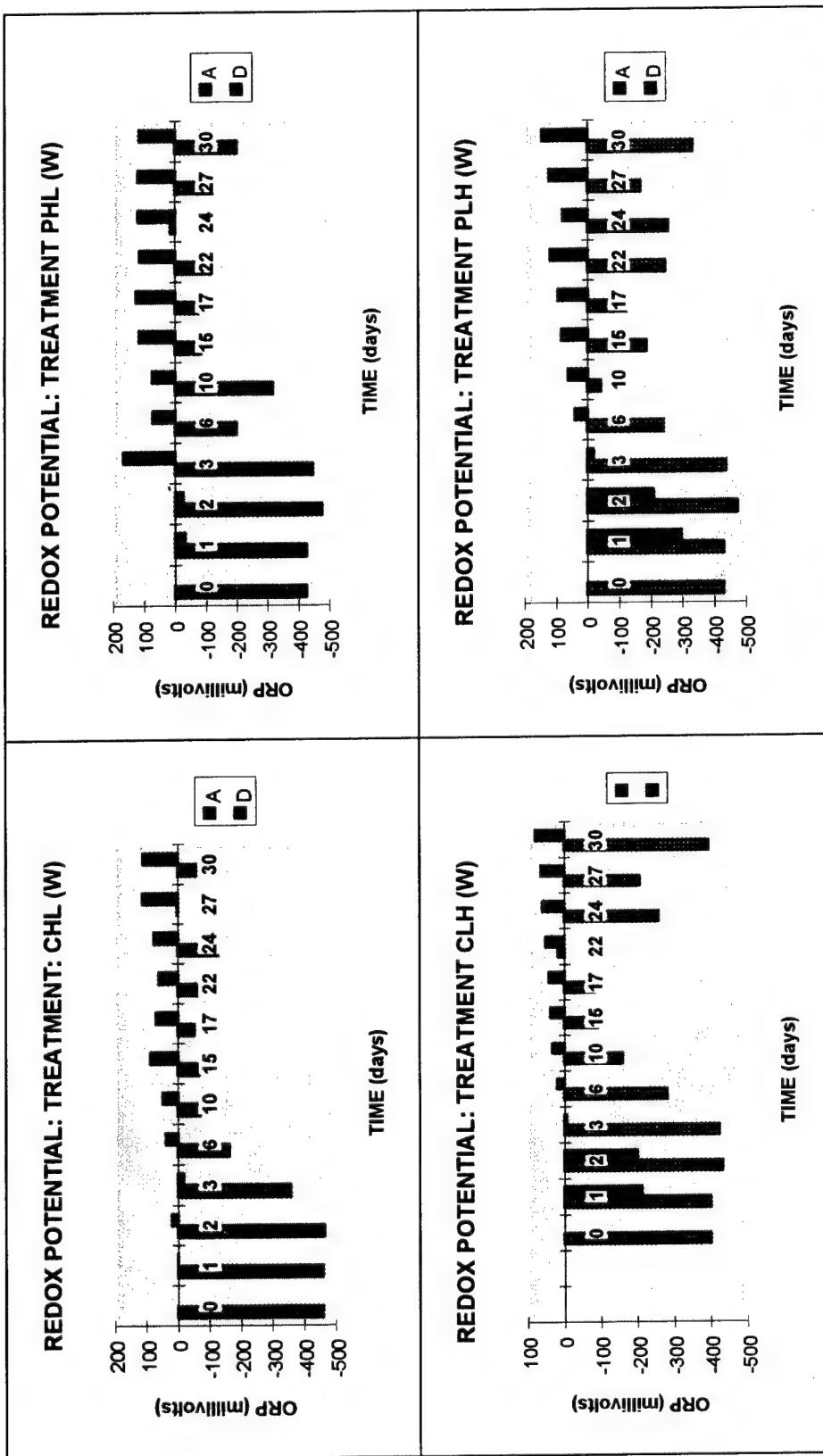


Figure 3-6
Redox potential as a function of wetland treatment and time for: CHL(W), CLH(W), PHL(W), and PLH(W).

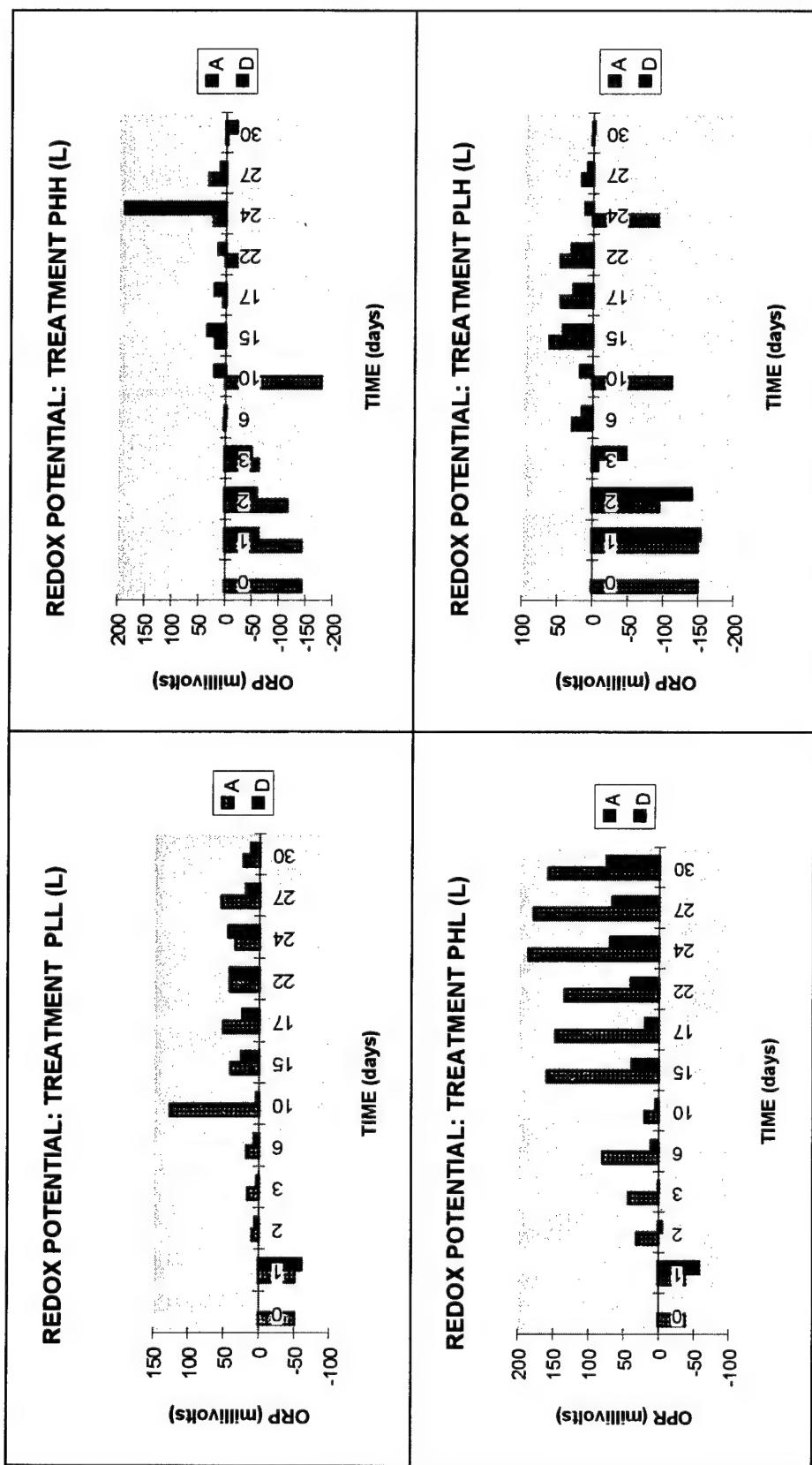


Figure 3-7

Redox potential as a function of lagoon treatments and time for: PLL(L), PHL(L), PHH(L), and PLH(L).

several important points:

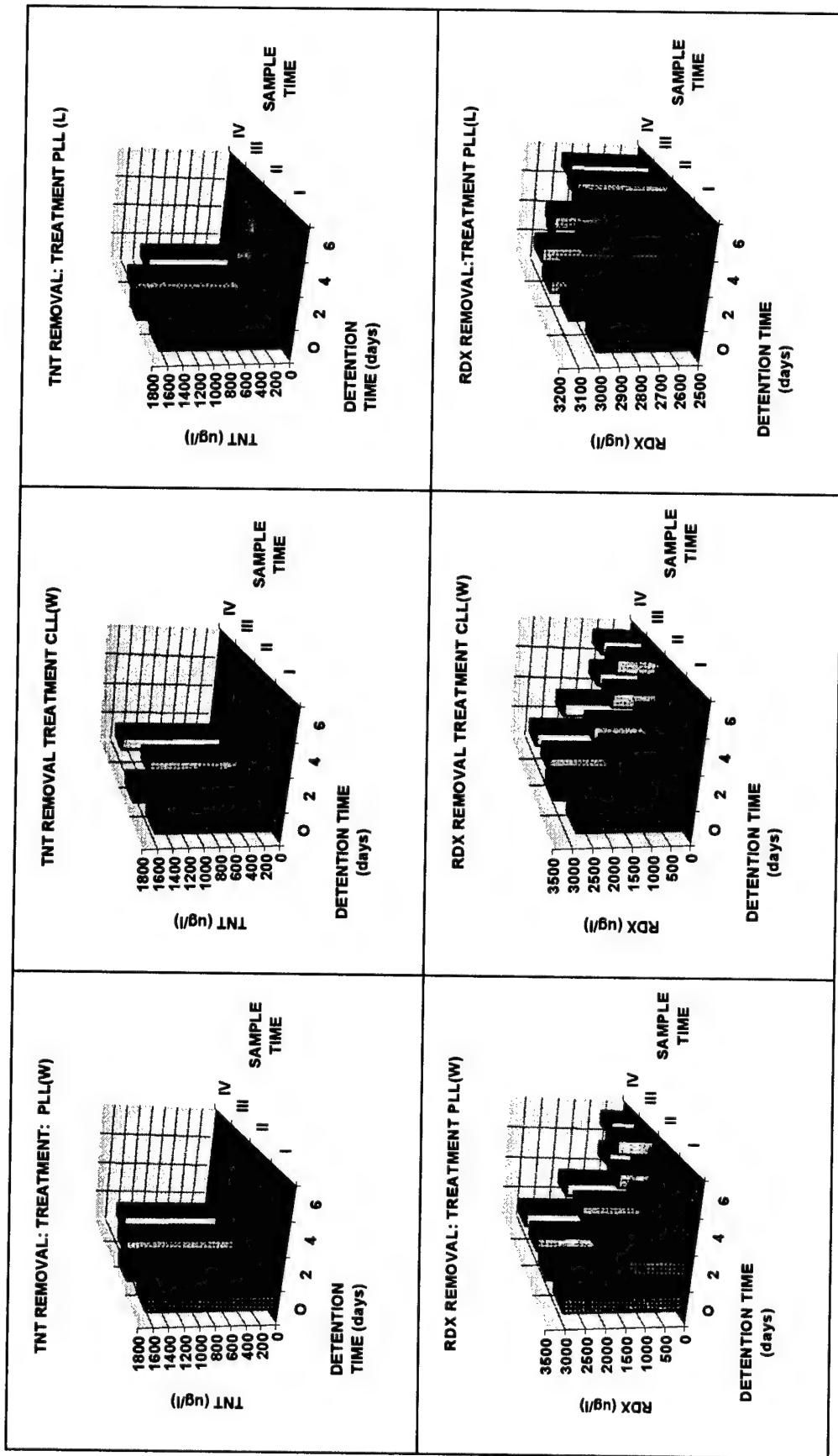
- High fertility treatments (700 mg/l MRS), in wetland treatments resulted in lower redox conditions (-400 to -500) for a longer period of time than low fertility treatment (350 mg/l MRS). As will be seen later, low redox conditions are required for removal of several types of munitions and their by-products.
- Both species and plant density affected redox potential. Various organic compounds are known to be released by the roots into the rhizosphere and thus contribute carbon to the system. The carbon is subsequently oxidized and helps to maintain low redox conditions. This aspect of the systems ecology helps to sustain low redox values and the treatments efficacy. In the lagoon system there is also input of plant-based carbon, however there is adequate oxygen from surface diffusion and photosynthesis and thus the system stays aerobic.
- The reciprocating action (cells C and D), infused oxygen into the system, thus facilitating development of aerobic biofilms and subsequent aerobic removal of excess carbon, nutrients and explosives by-products.

3.3 Explosives and Byproduct Removal

3.3.1 TNT and RDX

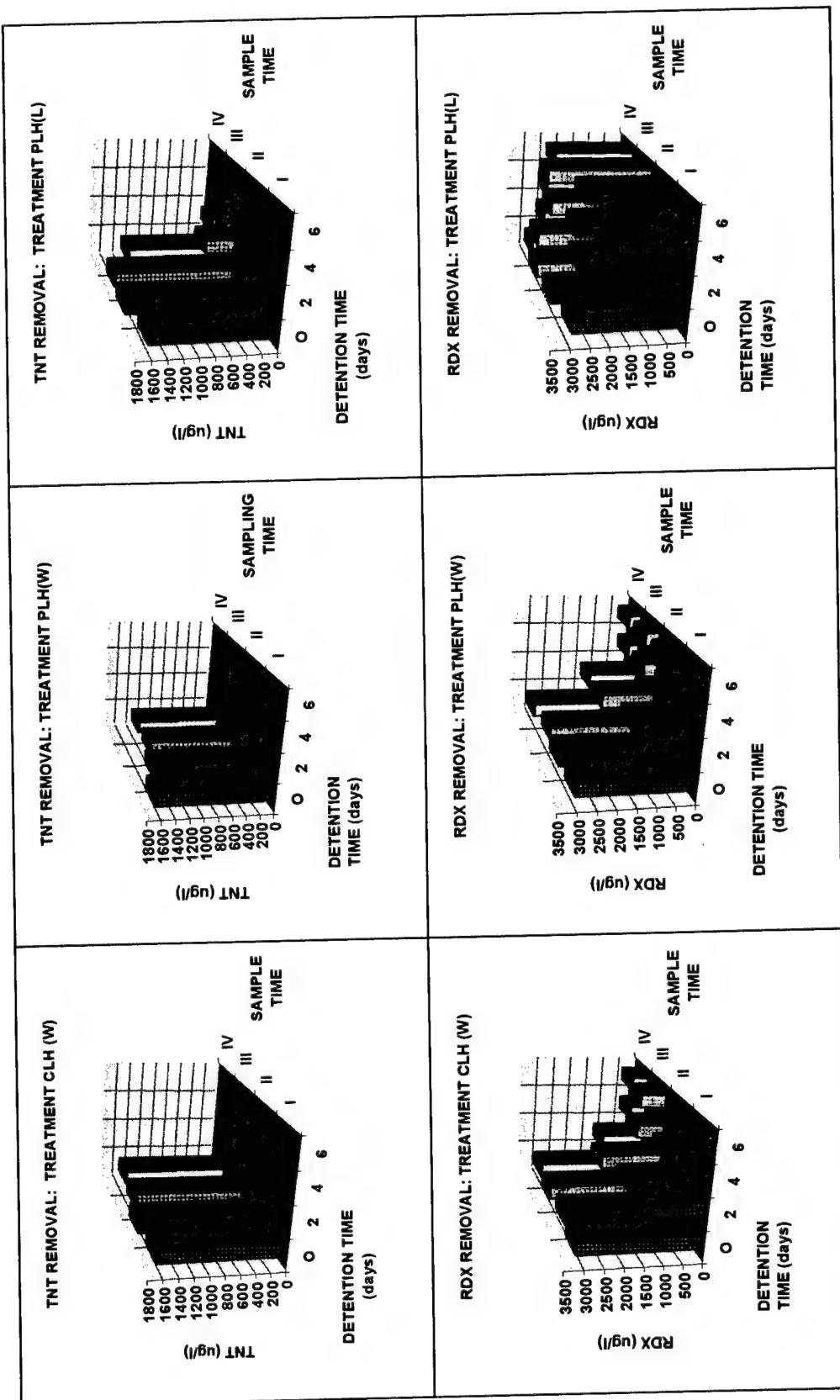
As in the previous microcosm (batch) study, TNT was rapidly removed from microcosms, irrespective of the treatment (Figures 3-8, 3-9, 3-10, and 3-11). Influent concentrations averaged 1600 ug/l, and were removed to below detection limits within 2 days in wetland microcosms; and within 4 days in lagoon treatments. However, there was a tendency for low concentrations of TNT to persist in some of the lagoon treatments beyond six days post fertilization (Figure 3-10).

RDX removal was rapid during the first six days post-fertilization, especially in the high fertility treatments. Examination of Figures 3-8 through 3-11 reveals rapid removal of RDX in all wetland treatments after initial fertilization, with a progressive lessening of efficacy with time, especially in the low fertility treatments (sample times I, II, III, and IV representing days 6, 10, 20, and 30).



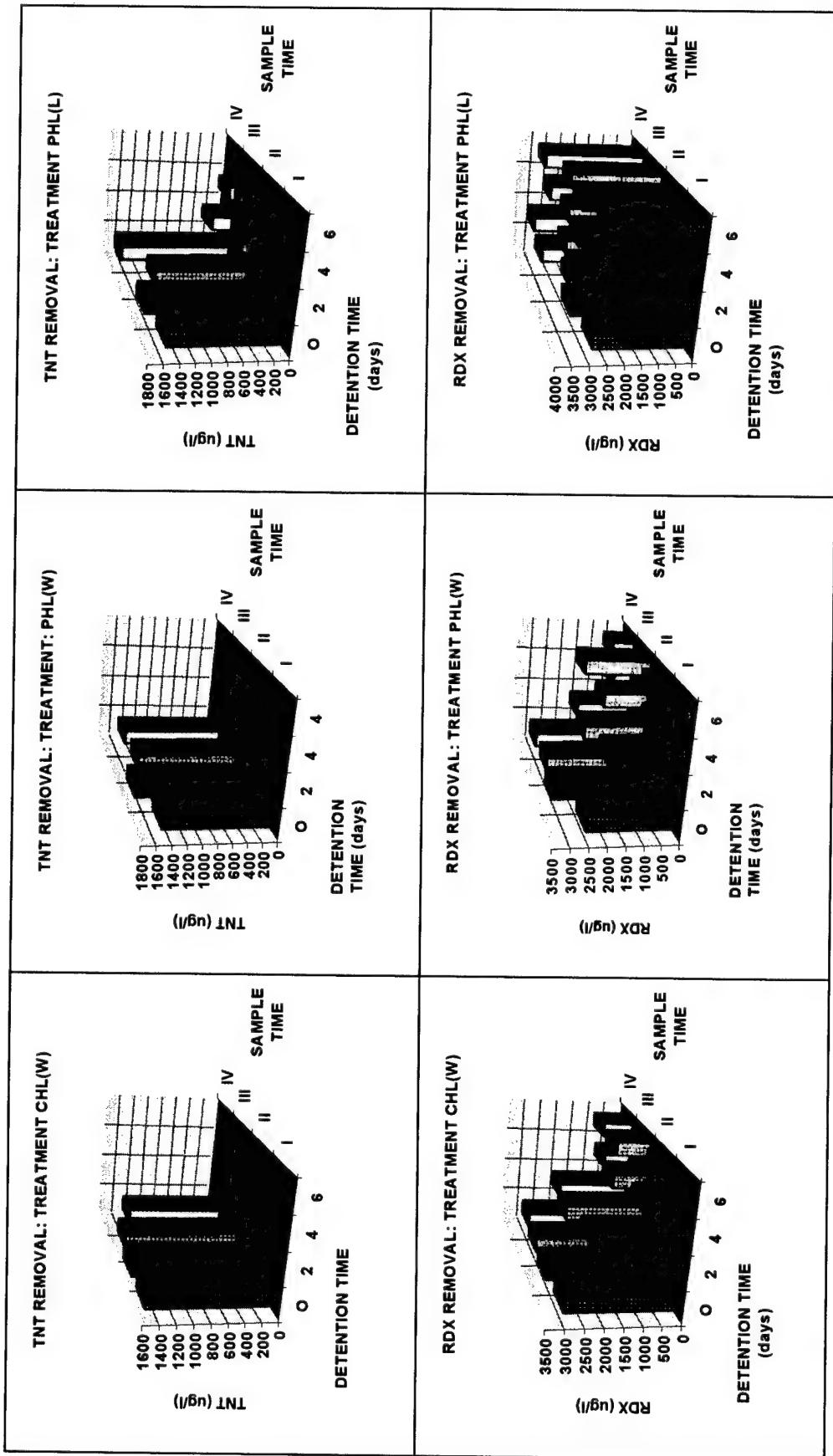
Notes: 1) Detention time 0-6 days; sample times at day 6 (I), 10 (II), 20 (III), and 30 (IV).
 2) Missing data for two cells in RDX graphic, treatment PLL(L)

Figure 3-8
Removal of TNT and RDX as a Function of Treatment for: CLL(W), PLL (W), and PLL(L).



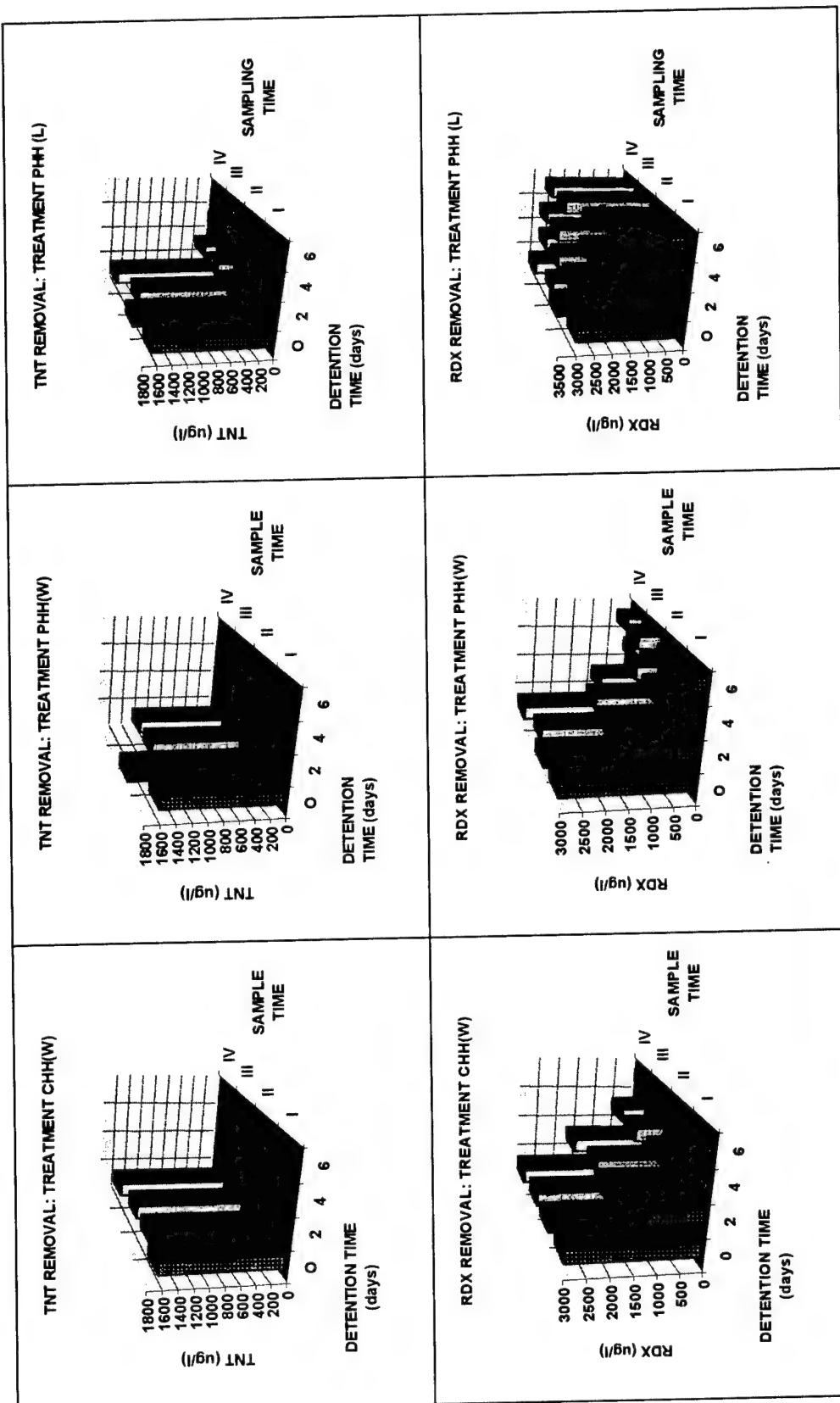
Note: 1). Detention time 0-6 days; sample times at day 6 (I) , 10 (II) , 20 (III), and 30 (IV).

Figure 3-9
Removal of TNT and RDX as a Function of Treatment for: CLH(W), PLH (W), and PLH(L).



Note: 1). Detention time 0-6 days; sample times at day 6 (I) , 10 (II) , 20 (III), and 30 (IV).

Figure 3-10 Removal of TNT and RDX as a Function of Treatment for: CHL(W), PHL (W), and PHL(L).



Note: 1). Detention time 0-6 days; sample times at day 6 (I) , 10 (II) , 20 (III), and 30 (IV).

Figure 3-11
Removal of TNT and RDX as a Function of Treatment for: CHH(W), PHH (W), and PHH(L).

Figure 3-12 illustrates treatment efficiencies over time, as measured by K-values.

RDX influent concentrations averaged near (3000 ug/l), and were reduced to approximately 82 ppb in treatment CHH (W) after 4 to 6 days of retention (Figure 3-11). Treatment PHH (W) also reduced RDX substantially, to levels approaching 68 ppb. However, removal rates slowed progressively from day six to day twenty (Figures 3-8 to 3-11). Subsequent fertilization on day twenty did not result in a significant decrease in RDX concentrations, and may have been due to an inappropriate fertilization method. It is felt that better results will be obtained by step-feeding the fertilizer into the treatment train at different locations along its length, rather than inputting all of the concentrated fertilizer solution at the influent end of the system.

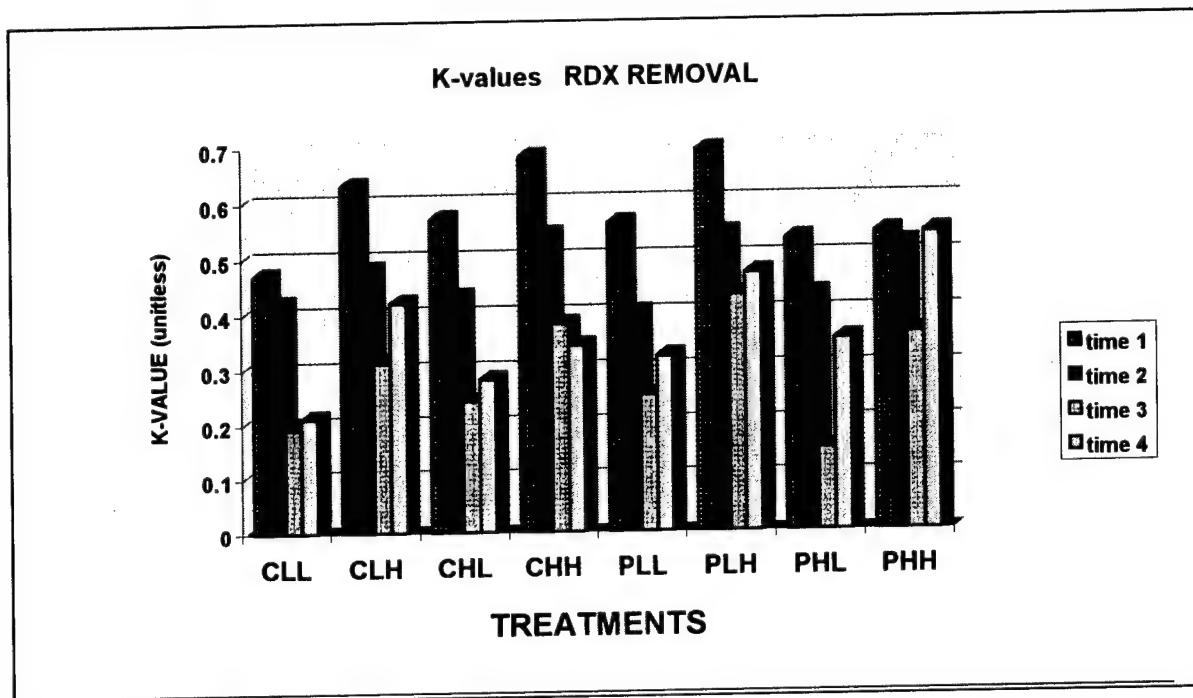
The lagoon treatments (L), were ineffective at removing RDX, irrespective of fertilization and planting regime. Even at high fertility and high planting density, RDX concentrations only decreased from 2900 ug/l to 2700 ug/l after six days of retention.

RDX removal was significantly influenced by redox level, with best removal rates achieved at low levels of redox (ORP< -250). High correlation was achieved between average redox levels and average RDX removal rates ($r= 0.89$), indicating that approximately 80 percent of the variation in RDX removal could be accounted for by variation in redox potential ($R^2 = 0.79$).

3.3.2 TNB and HMX

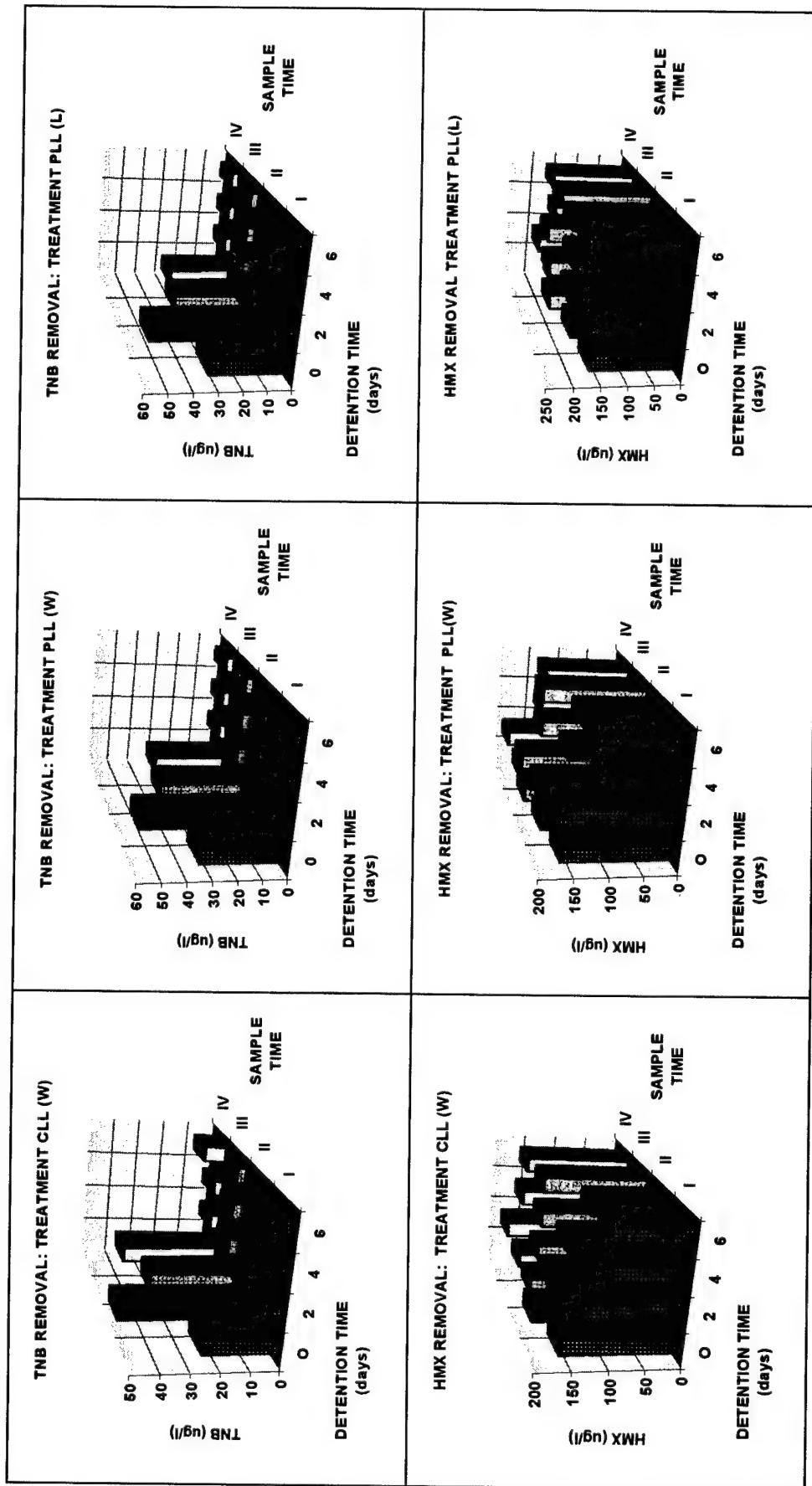
Influent TNB concentrations ranged from 20 to 50 ppb (ug/l). Wetlands, irrespective of treatment, effectively removed TNB to below detection limits within the first two days of retention, while lagoons often required 4 days (Figures 3-13, 3-14, 3-15, and 3-16). On one occasion there was a small spike subsequent to TNB being removed below detection limits (Figure 3-15).

Influent concentration of HMX ranged from 150 to 160 ppb. No treatment effectively removed HMX to less than 50 ppb. There was a tendency for removal to be more effective soon after fertilization, but the efficacy dropped off with time. Additional studies should be undertaken to



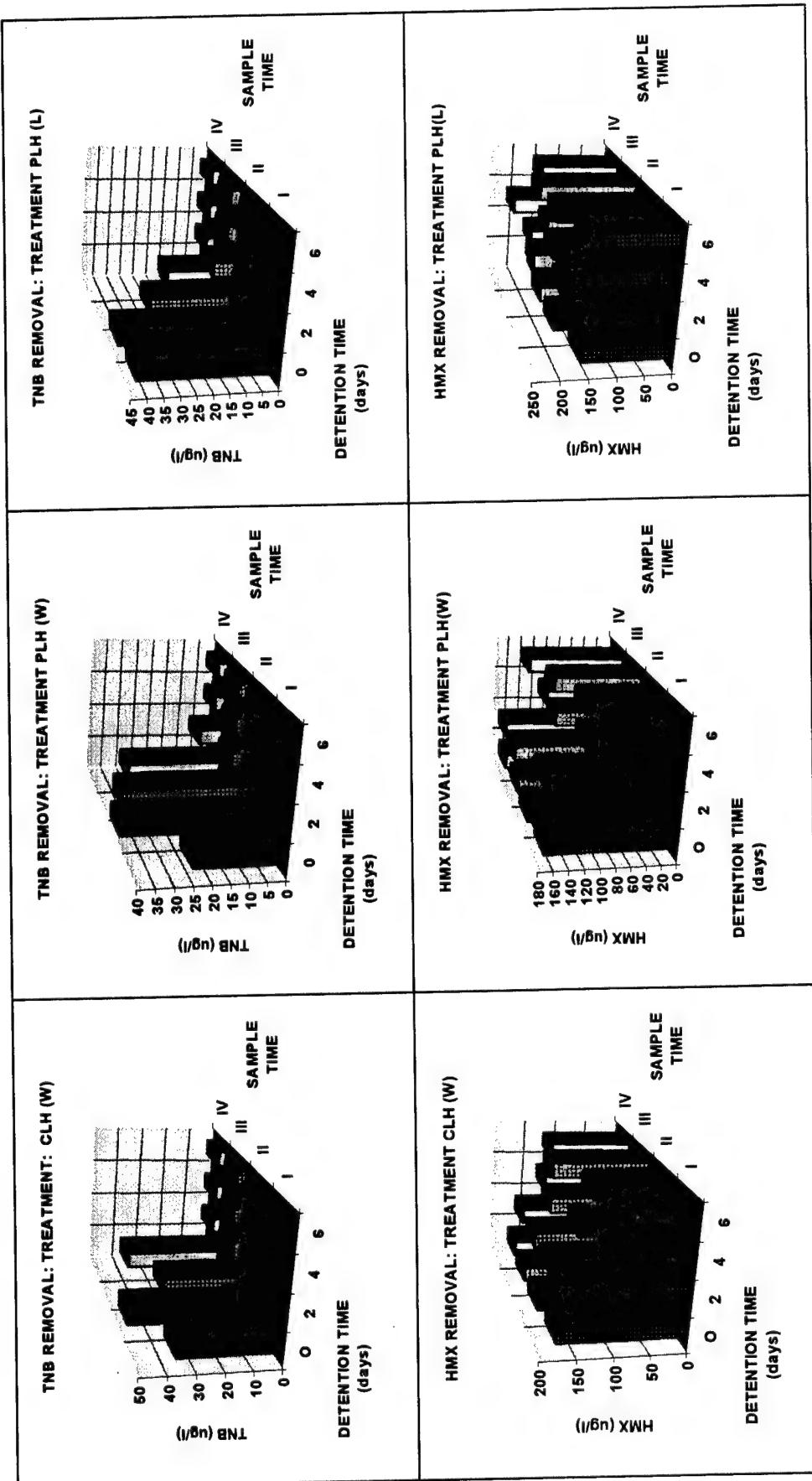
Note: Notice marginal to moderate improvement in removal rates following fertilization on day 20 (time = 3).

Figure 3-12
Relationship between K-value and treatments as a function of time.



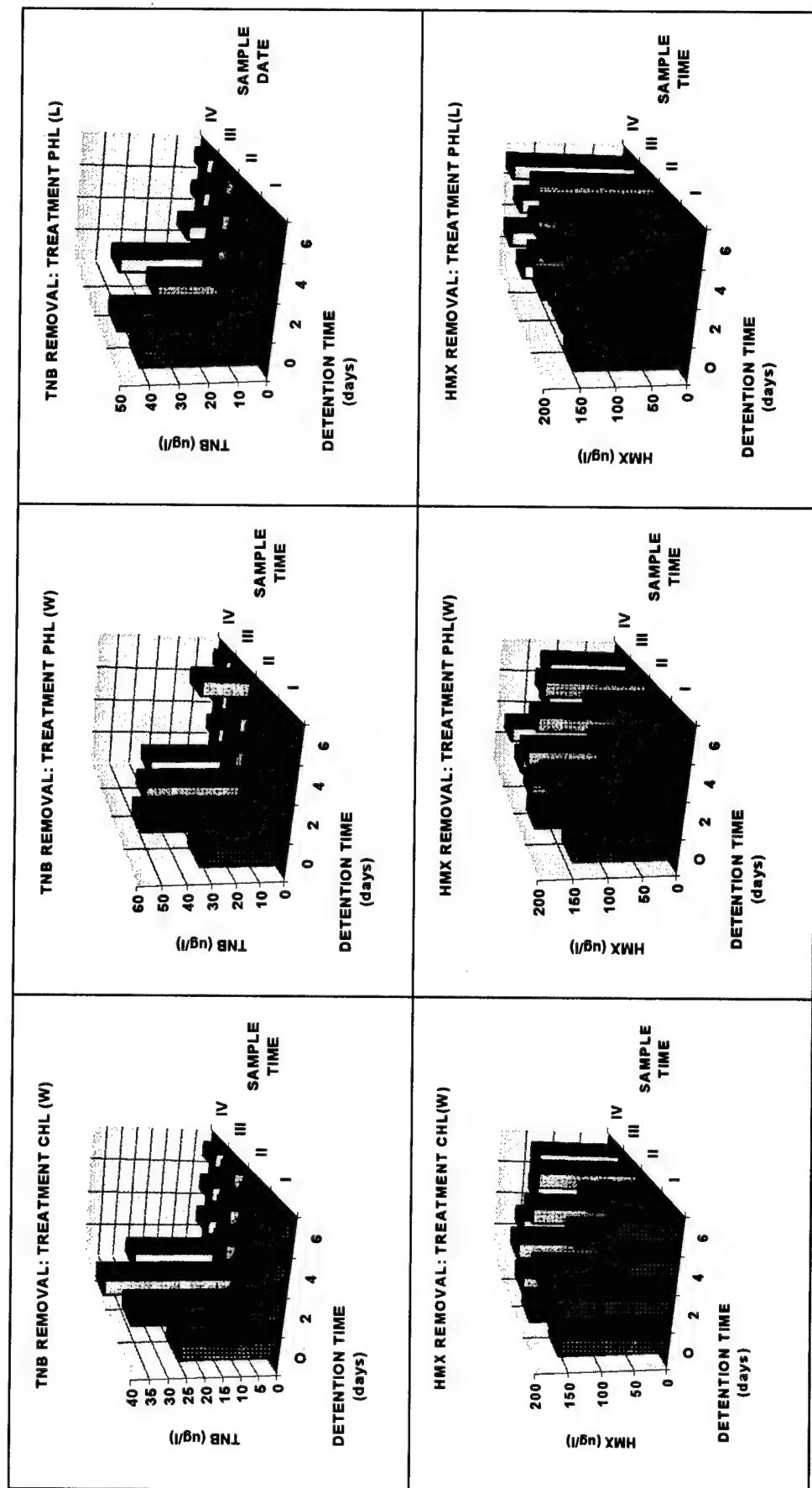
Note: 1). Detention time 0-6 days; sample times at day 6 (I), 10 (II), 20 (III), and 30 (IV).

Figure 3-13
Removal of TNB and HMX as a Function of Treatment for: CLL(W), PLL (W), and PLL(L).



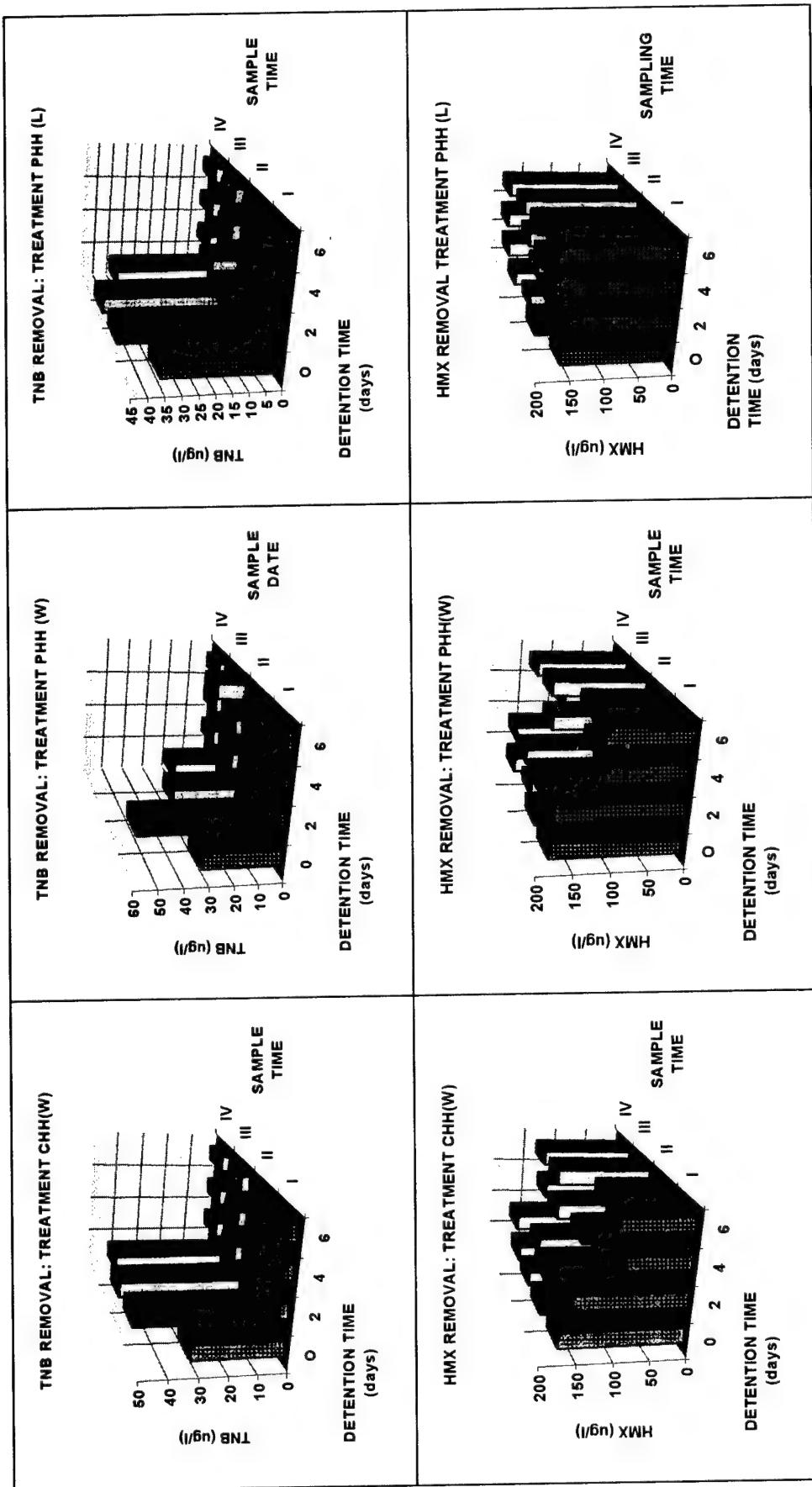
Note: 1). Detention time 0-6 days; sample times at day 6 (I) , 10 (II) , 20 (III), and 30 (IV).

Figure 3-14
Removal of TNB and HMX as a Function of Treatment for: CLH(W), PLH (W), and PLH(L).



Note: 1) Detention time 0-6 days; sample times at day 6 (I), 10 (II), 20 (III), and 30 (IV).

Figure 3-15
Removal of TNB and HMX as a Function of Treatment for: CHL(W), PHL (W), and PHL(L).



Note: 1) Detention time 0-6 days; sample times at day 6 (I), 10 (II), 20 (III), and 30 (IV).

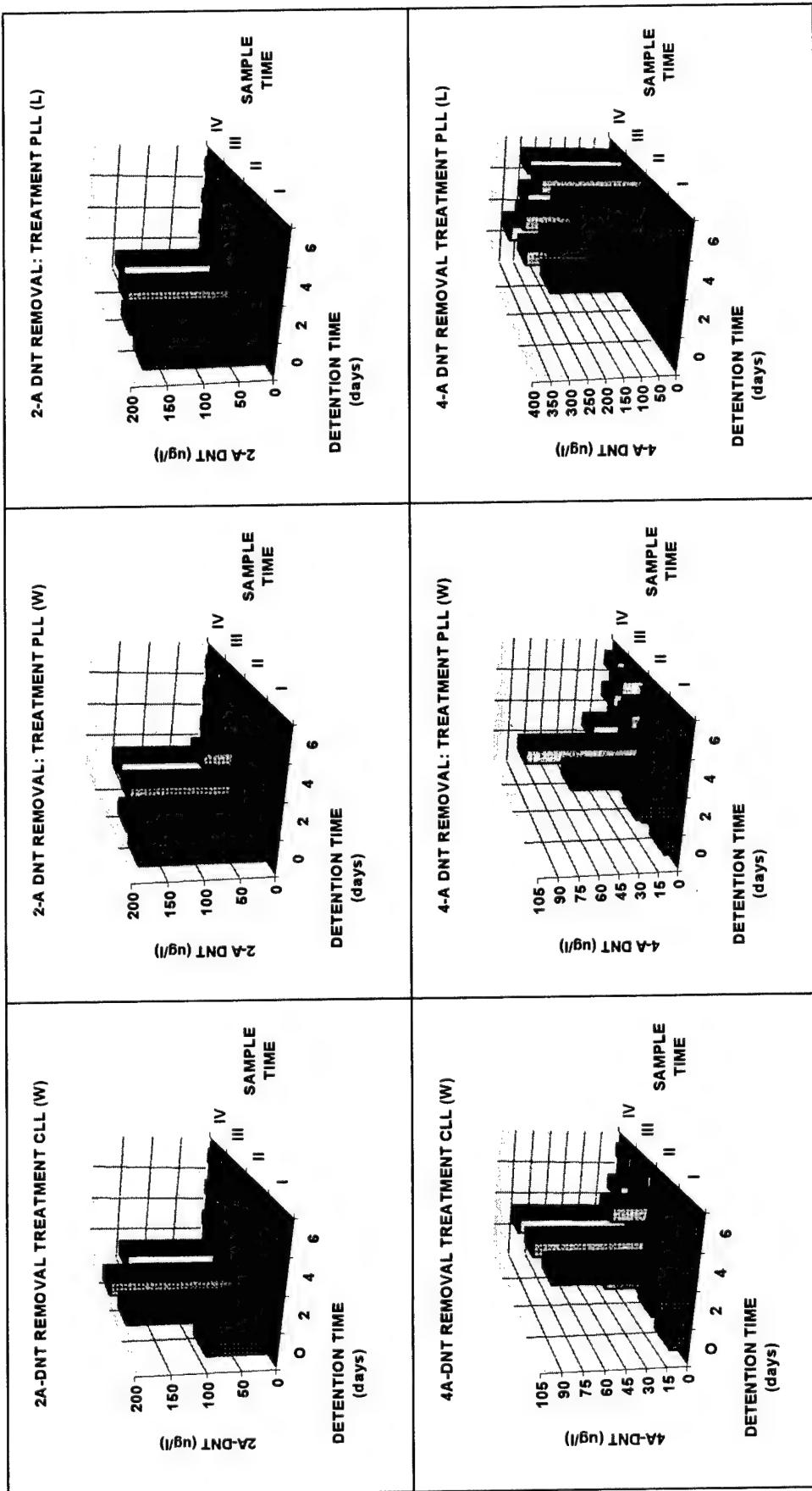
Figure 3-16
Removal of TNB and HMX as a Function of Treatment for: CHH(W), PHH (W), and PHH(L).

determine if HMX removal could be improved at even lower redox levels. HMX concentrations actually increased in some of the lagoon treatments probably as a result of very low removal rates and high evapotranspiration rates.

3.3 2-A DNT and 4-A DNT

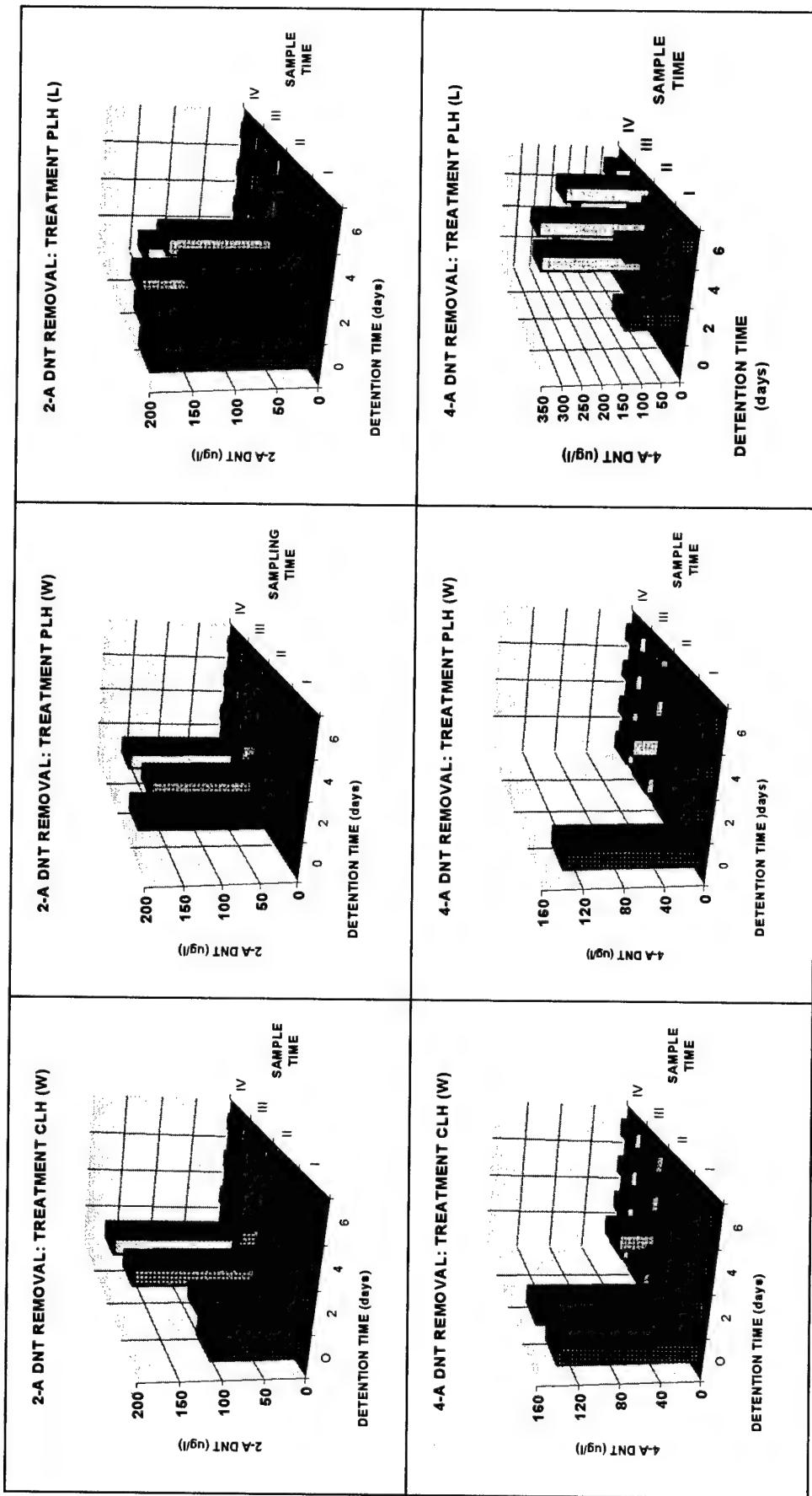
2-A DNT influent concentrations ranged from 100 to near 200 ppb. All treatments, with few exceptions, removed this by-product to below detection limits within 2 to 4 days (Figures 3-17, 3-18, 3-19, and 3-20). There was an occasional spike (Figure 3-19), which occurred on day 20, indicating that carbon limitation may be a factor (low carbon and elevated redox conditions may not be conducive to biological removal). Again, there was a tendency for the lagoon systems to remove 2-A DNT at a slower rate than their counterpart wetland system.

Concentrations of 4A-DNT ranged widely during the 30 day study, and seemed to be most effectively removed in wetland systems at high fertility rates. Lagoon systems at the low fertility rate had effluent concentration in excess of 250 ppb (Figures 3-17 and 3-19). 4A-DNT is a by-product of TNT degradation and 4A-DNT concentrations increased to high levels in the lagoon systems as TNT was removed. However, net removal of 4A-DNT in the lagoon systems was slow; thus leading to high discharge concentrations. In wetland systems, TNT was also rapidly degraded, but 4A-DNT concentrations never rose to levels experienced in the lagoons. We surmise this occurred because 4A-DNT removal rates were nearly as rapid as the rates of formation.



Note: 1). Detention time 0-6 days; sample times at day 6 (I) , 10 (II) , 20 (III), and 30 (IV).

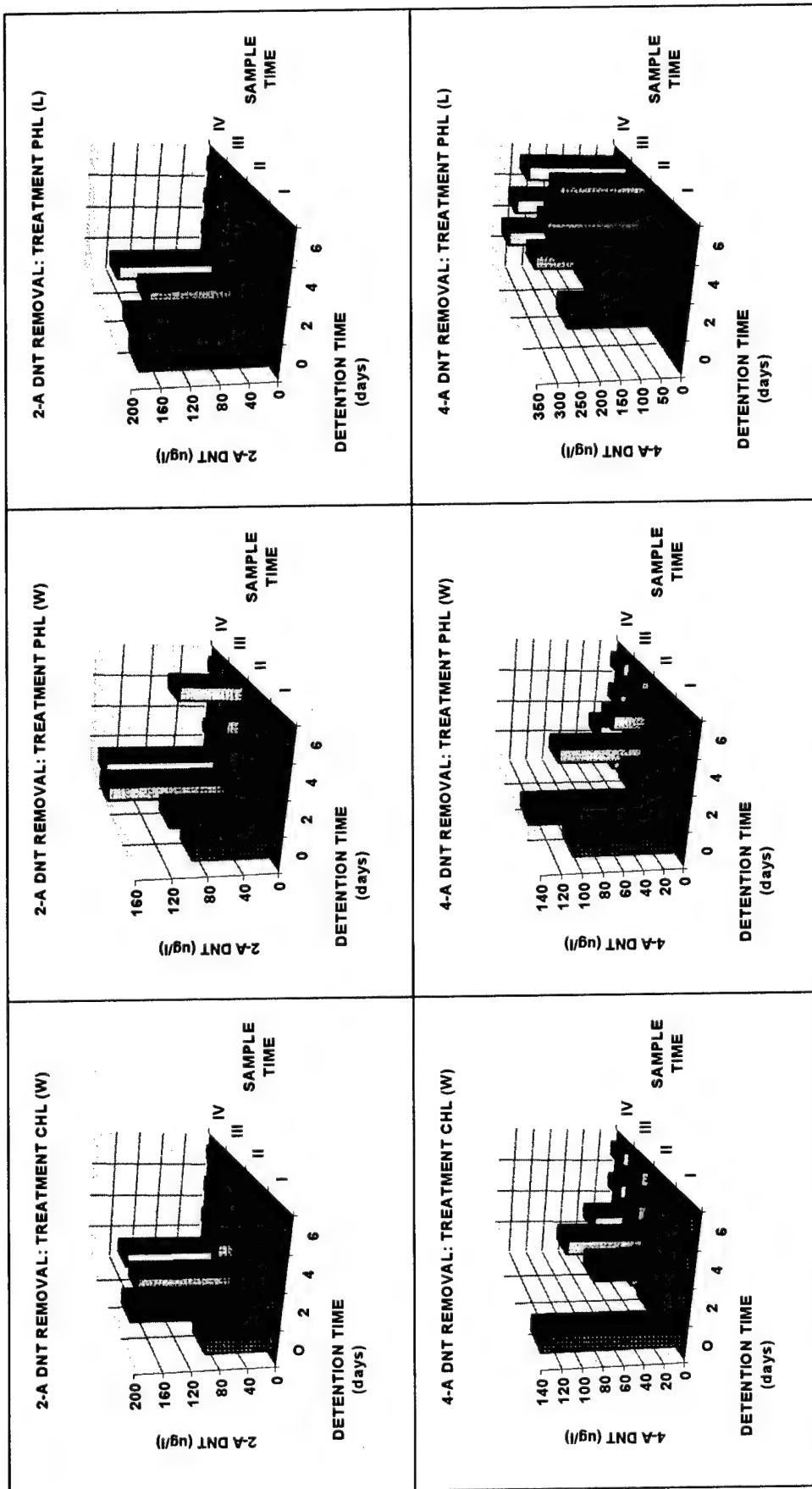
Figure 3-17
Removal of 2A-DNT and 4A-DNT as a Function of Treatment for : CLL(W), PLL (W), and PLL(L).



Note: 1). Detention time 0-6 days; sample times at day 6 (I), 10 (II), 20 (III), and 30 (IV).

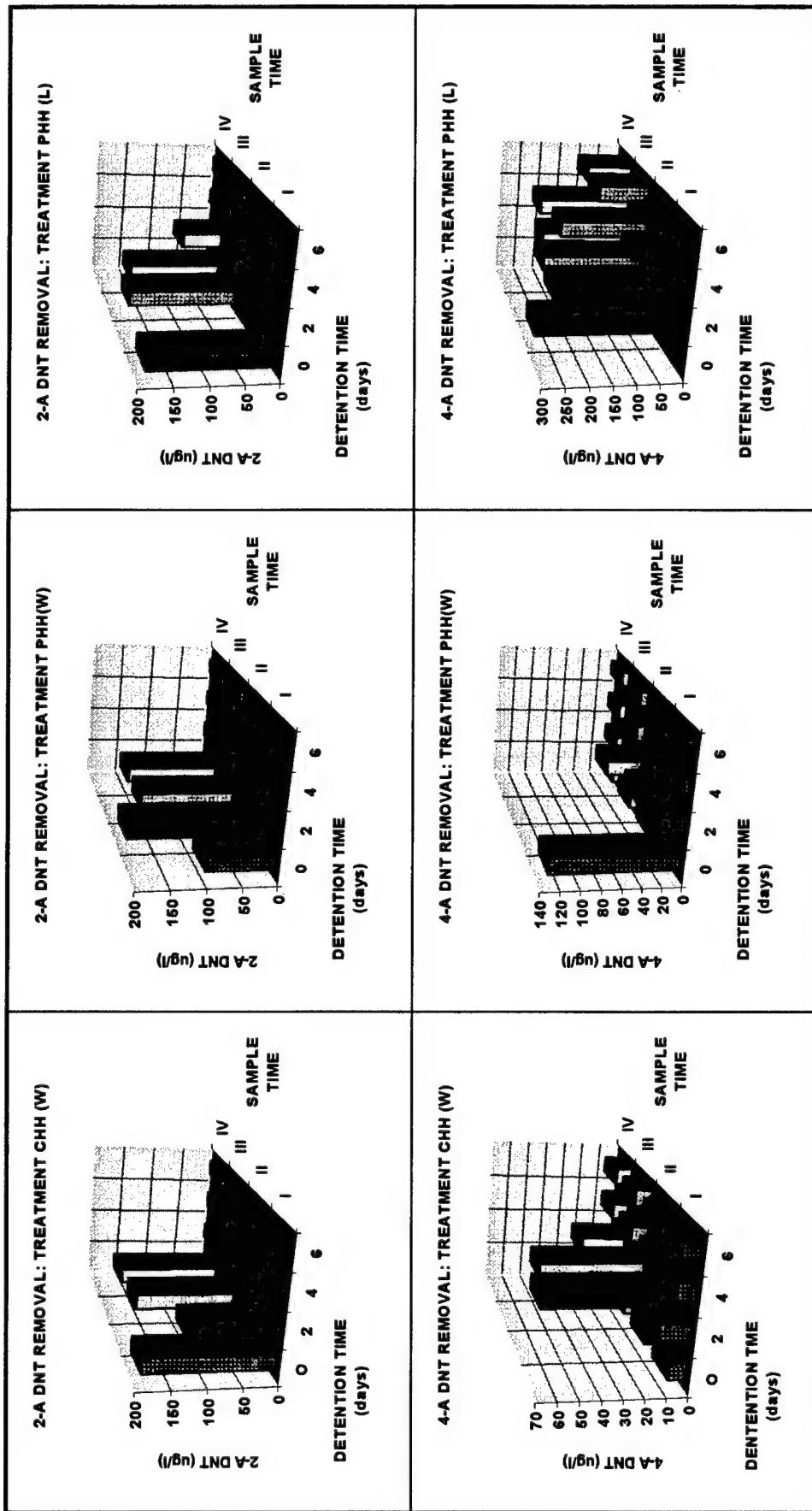
Figure 3-18

Removal of 2A-DNT and 4A-DNT as a Function of Treatment for: CLH(W), PLH (W), and PLH(L).



Note: 1). Detention time 0-6 days; sample times at day 6 (I), 10 (II), 20 (III), and 30 (IV).

Figure 3-19
Removal of 2A-DNT and 4A-DNT as a Function of Treatment for: CHL(W), PHL (W), and PHL(L).



Note: 1). Detention time 0-6 days; sample times at day 6 (I), 10 (II), 20 (III), and 30 (IV).

Figure 3-20
Removal of 2A-DNT and 4A-DNT as a Function of Treatment for: CHH(W), PHH (W), and PHH(L).

SECTION 4.0

CONCLUSIONS

This study further validates the findings of Study I, in which it was found that TNT, TNB, RDX, 2A-DNT and 4A-DNT could be effectively removed in wetland systems in which redox conditions were maintained below -250. This study also demonstrated that lagoons, irrespective of fertility level or plant density, were not able to remove RDX or 4A-DNT to levels required for discharge. The major factor impacting shallow lagoon systems is the import of dissolved oxygen from diffusion and photosynthesis, which precludes development of anaerobic zones.

Detailed analysis of plant production data, fertilization rates and redox potential indicates that fertilization, plant biomass and planting strategy (species selection and planting location), may play an important role in the sustainability of wetlands for treating munitions-contaminated groundwater.

Tracking redox potential internal to the system and over time may be an excellent management technique to monitor when and how best to fertilize the system to maintain low redox conditions and treatment efficacy.

Reciprocation was an effective strategy for removing COD, stabilizing pH, enhancing root to shoot ratios, and elevating dissolved oxygen levels to concentrations adequate for discharge.

SECTION 5.0

ACKNOWLEDGMENTS

Thanks is expressed to Jerry Clayton, Michael Bulls, Jerry Berry, Danny Williams, Eddie White, and Johnny Matlock for their diligent efforts in maintaining the experimental cells and making the study a success.

Thanks is also expressed to Richard Almond, the project manager, and Joseph Hoagland for their contributed ideas and direction to the project.

NATURAL ATTENUATION REMEDIATION OF LEAD-CONTAMINATED SOILS AT A FORMER OPEN BURNING PROPELLANT DISPOSAL SITE

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ABSTRACT

Lead-contaminated surface soils at an eleven-acre former open-burning propellant disposal site at the Badger Army Ammunition Plant were scheduled for remediation by phosphate-addition soil stabilization and soil cover construction. Laboratory treatability tests performed to select an effective mix of stabilization compounds suggested that native soils (a 5 - 7 foot thick loess deposit) underlying the contaminated topsoil had a high capacity to immobilize/attenuate lead naturally, without the addition of artificial chemical stabilizers. This initial testing showed that over 99% of dissolved lead content was removed from leachates contacted with the underlying soils, up to a leachate lead content of over 10,000 $\mu\text{g/l}$. Before further studies were undertaken to support remediation through natural attenuation for this site, soil borings were installed on a 100' grid to establish the presence of the attenuating loess layer across the entire site. Then, leachates created from contaminated site soils through the Synthetic Precipitation Leaching Procedure (SPLP) were contacted with underlying attenuating soil. Pre-contact and post-contact leachate lead concentrations were tracked to determine the level of attenuation achieved. The SPLP leachates, which characteristically had a low dissolved lead content, were also spiked with higher concentrations of lead (up to 10,000 $\mu\text{g/l}$). Using these spiked leachates, the soil's attenuation capacity at higher lead levels was evaluated. The results showed that the underlying soils had over 20,000 times more capacity to attenuate dissolved lead than the contaminated soils had capacity to generate dissolved lead. Securing approval from regulators to forego chemical stabilization/soil cover in favor of natural attenuation/soil cover was a rigorous process. Like most military installations, remedial activities at Badger AAP are closely scrutinized by regulators and a local environmental group. Therefore, regulatory personnel were very cautious about granting this approval which represented a significant change from the soil stabilization plan previously approved. Documentation of laboratory and field studies described above was submitted as well as long-term groundwater data showing no indication of lead impact from overlying soils, and detailed soil analysis confirming that the lead contamination had been naturally immobilized in the upper six inches of top

soil. Approval was granted on the condition that two small collection lysimeters be installed under the contaminated soils to confirm that infiltrating precipitation is not leaching detrimental amounts of lead from the attenuating soils. Our ability to obtain approval of the "natural attenuation" alternative for these contaminated soils not only represents a savings of taxpayer dollars on this particular project due to the elimination of stabilization costs, but also sets a precedent for regulatory consideration of practical alternatives to expensive remedial technologies proposed for contaminated sites statewide.

1. INTRODUCTION

Natural attenuation of contaminants in soils and groundwater is at the forefront of emerging remedial technologies. Whereas natural attenuation used to be regarded as the equivalent of a "no action" alternative, it is now realized that nature's physical and chemical processes can go far to moderate the effects of anthropogenic contaminants. When natural attenuation can be proven and used as the remedial action for a contaminated site, savings in funding expenditures can be realized without compromising protection of human health and the environment. At this early stage of the development of natural attenuation as a remedial method, regulators are often hesitant to approve natural attenuation remedial actions. This paper details the investigation and documentation that were necessary to successfully secure regulatory approval for the natural attenuation of lead in surface soils at a former open burning disposal site.

1.1 INSTALLATION HISTORY AND BACKGROUND

The Badger Army Ammunition Plant (BAAP) is situated on 7354 acres, 30 miles north of Madison, Wisconsin. Site boundaries include U. S. Highway 12 on the west, Devil's Lake State Park on the north, and farmland on the south and east.

1.1.1 Installation Activities and Regulatory Environment

During World War II, and the Korean and Vietnam Conflicts, BAAP produced rocket and small arms propellants and propellant intermediates such as nitroglycerine, nitric acid, and sulfuric acid. Badger has been in "stand-by" status since 1975 when the focus of operations changed from propellant production to the investigation and remediation of soils and groundwater contaminated by production activities. These remedial investigations and actions are monitored by the Wisconsin Department of Natural Resources (WDNR) and the United States Environmental Protection Agency, with the WDNR taking the regulatory lead.

1.2 RACETRACK AREA BACKGROUND

The subject site for this paper is a portion of the Propellant Burning Ground in the southwest quarter of the installation, one of several solid waste management units on the facility. The Propellant Burning Ground contains four separate sites requiring remediation. We will focus on the Racetrack Area site, named for the oval gravel road that dominates the site topography.

1.2.1 Racetrack Area Activities

The eleven-acre Racetrack Area of the Propellant Burning Ground at BAAP was the site of open burning disposal of off-specification propellants and propellant wastes including nitrocellulose, BALL POWDER®, nitroglycerine-containing compounds and waste propellant paste. Initially, wastes were spread and burned directly on the ground surface. Later, open steel dishes and gas-fired grills were installed to perform burning disposal operations.

1.2.2 Contaminants and Contaminant Source Locations

Within the Racetrack Area there are several separate sources of contaminants: burning pads on the western side of the gravel oval, burning plates on the eastern side of the gravel oval, three small refuse pits adjacent to the southeast corner of the gravel oval, and the open burning on bare ground over most of the eleven-acre area.

As a result of propellant and propellant-waste burning activities at these Racetrack sites, surface soils contained propellant residues (2,4 and 2,6-dinitrotoluene) and elevated levels of lead. Lead contamination was the primary concern, with dinitrotoluene presenting a concern limited to the burning pad area. Soils were impacted to a depth of approximately six inches.

1.2.3 Site Geology and Hydrogeology

Immediately beneath the six inches of contaminated surface soils a five to seven foot thick layer of lean clay exists. This clay was deposited as loess at the base of the terminal moraine to just to the east of the Propellant Burning Ground. (This is the terminal moraine of the Green Bay Lobe of the Lake Michigan Glacier which last advanced during the Wisconsin Stage of glaciation.) Beneath the clay, outwash sands and gravels are found to a depth of 250 feet below ground surface where Eau Claire Formation bedrock is encountered. In this area, the Eau Claire Formation is a limey sandstone with thinly bedded shale. Groundwater occurs in the outwash at approximately 85 feet below ground surface.

1.3 RACETRACK REMEDIATION

Remediation of contaminated surface soils at the Racetrack took place in two phases.

Phase I included the removal of the most highly contaminated soils. Phase II addressed the remaining soils with lower levels of contamination.

1.3.1 Development of Clean-Up Standards

Clean-up goals for the lead-contaminated soils were developed based upon regional background lead levels. 30 mg/kg was determined to be the average background lead concentration for the area and that concentration became the clean-up goal. Because regulatory agencies felt that an in-situ remedial technique (soil stabilization) should be used at the site, a performance standard was also developed. Leachate from post-action/post-treatment soils remaining on the site was to contain no more than 15 $\mu\text{g/l}$ lead when subjected to the Synthetic Precipitation Leaching Procedure (SPLP). 15 $\mu\text{g/l}$ is the Wisconsin Enforcement Standard for lead in groundwater; concentrations below this level are considered protective of human health and the environment.

1.3.2 Phase I Remedial Action

Phase I of the remedial action involved the removal and decontamination of one burning dish and removal of the two concrete burning pads. After these items were decommissioned, soils containing 2,4 and 2,6-dinitrotoluene and having lead levels exceeding TCLP maximums were excavated. These soils were located on the western side of the gravel oval where burning pads had been located.

1.3.3 Phase II Remedial Action - Initial Plan

The remainder of the soils containing elevated lead levels, were to be remediated through phosphate-addition soil stabilization to immobilize lead followed by the construction of a 30-inch soil cover over the stabilized soils to provide a barrier between stabilized soils and ecological receptors, particularly burrowing animals. This action was named as the preferred alternative in the feasibility study for the site and was subsequently approved by regulators as the remedial action that would be performed.

1.4 TREATABILITY TESTING AND SUPPORT FOR NATURAL ATTENUATION

Treatability tests were performed to develop an effective chemical stabilization mixture for the affected soils. Results of these initial studies suggested that attenuation/immobilization of lead was occurring naturally in soils at the site. Further testing verified the conclusions of the initial study and a document supporting modification of the remedial method from soil stabilization/soil cover to natural attenuation/soil cover was compiled and submitted to regulators for approval.

1.4.1 Initial Treatability Study

The initial treatability study was designed to develop the chemical mix to be used to stabilized the remaining lead-contaminated soils. Results from a portion of this study

indicated that the five to seven foot layer of lean clay directly under the contaminated soils was able to naturally immobilize lead without the addition of chemical stabilizers. SPLP leachates were created from lead-contaminated site soils, and these leachates were spiked with up to 10,000 $\mu\text{g/l}$ dissolved lead. These spiked leachates were then contacted with uncontaminated material from the lean clay layer. Contact with the lean clay removed over 99% of the dissolved lead from those spiked leachates. (See Table 1.)

TABLE 1. INITIAL TREATABILITY TEST SPIKED LEAD ATTENUATION RESULTS

Sample	Initial Lead Concentration	Attenuation Test Results (After Contact with Lean Clay)	
		Lead Concentration	Percent Removal
+ 1,000 $\mu\text{g/l}$ lead	1,031 $\mu\text{g/l}$	8.7 $\mu\text{g/l}$	99.2
+ 5,000 $\mu\text{g/l}$ lead	5,031 $\mu\text{g/l}$	44 $\mu\text{g/l}$	99.1
+ 10,000 $\mu\text{g/l}$ lead	10,031 $\mu\text{g/l}$	28 $\mu\text{g/l}$	99.7

1.4.2 Support for Further Investigation of the Natural Attenuation Alternative

Three separate lines of evidence suggested that we take a close look at the possibility of utilizing natural attenuation at this site. First, results from the initial treatability study described above showed that native site soils could immobilize high levels of dissolved lead in infiltrating precipitation. Second, extensive soil data collected during the remedial investigation showed that lead from the surface had not migrated significantly; contamination was confined to the top six inches of the soil column. Finally, groundwater quality data collected for the area beneath the site over a period of eight years also showed no lead impacts.

1.4.3 Obstacles to Regulatory Approval of Natural Attenuation

When regulators were initially approached as to the possibility of obtaining approval for natural attenuation of contaminated soils in lieu of the already-approved chemical soil stabilization, they were pessimistic. As with most federal facilities, BAAP is a high-visibility site with a local environmental group focusing attention on remedial activities on the plant. Specifically, the Racetrack Area was the first remedial action for BAAP that would result in a site closure and, therefore, would be under high scrutiny. A second concern was that, if approved, this site would set a precedent for natural attenuation remediation approvals, resulting in requests for similar approvals across the state. Lastly, although Wisconsin Natural Resources Code did not specifically prohibit natural

attenuation as a remedial action alternative, the revisions to the code that would provide for natural attenuation's acceptance was under review by the state legislature, but not yet promulgated. However, the site data was convincing enough to move forward with further natural attenuation studies although regulatory approval did not appear promising.

1.4.4 Natural Attenuation Feasibility Study

Our study focusing on the feasibility of applying natural attenuation to the site had two main goals:

- Confirm the extent of the lean clay soil layer responsible for lead attenuation.
- Quantify the attenuation capacity of the underlying lean clay at locations across the site.

1.4.5 Confirmation of Lean Clay Layer Extent

Before further lab studies were undertaken, the extent of the lean clay soil layer needed to be defined. If the layer did not extend underneath the entire eleven-acre site, then some areas of the site would not be addressed by the attenuative capacity of that layer and we would not obtain approval. The presence of the layer was verified with soil borings performed on a 100-foot grid across the entire site.

1.4.6 Attenuation Capacity Quantification

Once the existence of the clay layer was established, a laboratory study was designed to evaluate the attenuative capacity of both the lean clay layer and underlying outwash sands. Three samples of lean clay were collected from different areas of the site to determine if attenuative capacities were consistent throughout the layer. One sample of underlying outwash sand was collected to check for any additional attenuation capacity it might provide.

These four soil samples were contacted with SPLP leachates prepared from contaminated site soils that were spiked with 1,000 $\mu\text{g/l}$ dissolved lead. 1,000 $\mu\text{g/l}$ was chosen as the spiking concentration purely for quantification of attenuation capacity at worst-case dissolved lead levels. Lead concentrations in SPLP leachates from site soils were much lower, typically under 20 $\mu\text{g/l}$.

Contact of spiked leachates with lean clay achieved dissolved lead removal rates of 96.8% - 98.0%. Contact with the underlying outwash sand resulted in a removal rate of 98.5%. (See Table 2.)

TABLE 2. NATURAL ATTENUATION FEASIBILITY STUDY RESULTS

Soil Sample	Spiked Lead Concentration Before Contact	Lead Concentration After Contact	% Attenuated
Lean Clay 1	1,000 $\mu\text{g/l}$	20 $\mu\text{g/l}$	98.0%
Lean Clay 2	1,000 $\mu\text{g/l}$	32 $\mu\text{g/l}$	96.8%
Lean Clay 3	1,000 $\mu\text{g/l}$	24 $\mu\text{g/l}$	97.6%
Underlying Sand	1,000 $\mu\text{g/l}$	15 $\mu\text{g/l}$	98.5%

1.4.7 Natural Attenuation Capacity of the Soil Column

The dissolved lead removal rates from the natural attenuation feasibility study were applied to the soil column to estimate the total attenuation capacity between the contaminated soils and the groundwater at 85 feet below ground surface. Figure 1 provides a summary of the estimates for the lean clay and outwash sand layers. It was estimated that the native soils had approximately 29,400 times more capacity to attenuate lead than contaminated surface soils had to generate dissolved lead.

1.5 DOCUMENTATION SUBMITTAL AND APPROVAL

A document detailing the results of the natural attenuation feasibility study, boring logs for the site's subsurface on a 100' grid, maps depicting residual lead levels, ecological risk assessment information, and a long-term monitoring proposal for site was assembled and submitted to the Wisconsin Department of Natural Resources for approval.

Approval was granted on the condition that two lysimeters be installed under the lean clay layer in areas of highest residual lead levels. These sampling points will monitor the dissolved lead content of any infiltrating precipitation passing through the lean clay layer and confirm the effectiveness of natural attenuation for these soils.

CONCLUSIONS

The reduction in cost and level of remedial effort achieved at this site through the application of natural attenuation of lead-contaminated soils is an example of what can be accomplished through innovative approaches to contaminant problems. Contamination situations that might be resolved with a lower level of effort without compromising human health or the environment should be actively sought and identified. When these sites are identified, regulators must be approached with innovative

FIGURE 1. NATURAL LEAD ATTENUATION CAPACITY OF SITE SOILS

Soil Description	Soil Depth	Hypothetical Lead Leaching Potential of Surface Soil (mg lead/m ² soil)	Lead Attenuation Capacity of Soil* (mg lead/m ² soil)	Comments
Surface Soil	6"	225	NA	
Subsurface soil (lean clay)	15"	NA	>312,000	~1,400 times the lead leaching potential of surface soil
Underlying soil (sand)	100"	NA	>6,235,000	~28,000 times the lead leaching potential of surface soil

* For entire soil column of 1 m² area.
 NA Not applicable.

proposals that provide in full the information and data they need to grant approval for remedial actions with reduced remedial costs.

**PRELIMINARY PERFORMANCE RESULTS FROM A ZERO
VALENT METAL REACTIVE WALL FOR THE PASSIVE TREATMENT
OF CHLORINATED ORGANIC COMPOUNDS IN GROUNDWATER**

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ABSTRACT

In an effort to improve the cost/performance for treatment of dissolved-phase chlorinated organics in groundwater, the U.S. Air Force demonstrated a zero-valent iron reactive wall at Lowry Air Force Base (AFB), Colorado. Chlorinated aliphatic hydrocarbons (CAHs) are degraded via a reductive dechlorination reaction involving the zero valent iron. Preliminary results indicate that all of the chlorinated species are rapidly degraded to concentrations below their quantitation limits. Reaction kinetics based on these preliminary results appear to be first order, and degradation rate constants are

presented for nine CAHs. Precipitation of iron salts was demonstrated through evaluation of geochemical parameters. Long-term remediation cost is presented and evaluated on the basis of CAH mass removed.

1. INTRODUCTION

CAHs (e.g., trichloroethene [TCE]) are the principal organic contaminants at many Air Force installations. The overall cost to the Air Force for remediating groundwater contaminated with CAHs by traditional pump and treat technology could become prohibitive, since operational costs will be accrued over a period of many years. Previous studies have indicated that CAHs dissolved in groundwater may be effectively degraded *in situ* when placed in contact with a zero-valent metal, such as iron. Several zero-valent iron reactive walls have successfully remediated groundwater in Canada and the United States. This paper discusses preliminary performance results for a zero-valent iron reactive treatment wall that was installed at a site at Lowry AFB to demonstrate the feasibility of this technology for use at other Air Force sites.

2. BACKGROUND

2.1 Description of the Technology

The degradation of CAHs in aqueous solution by zero-valent metals was recognized some time ago, but was not utilized for groundwater remediation until recently. Several authors have reported CAH degradation by using column reactors containing metal,^{1,2} in laboratory studies,³ and in a pilot-scale field demonstration.⁴ The zero-valent metal reactive wall is an *in situ* technology, which does not require the extraction and subsequent treatment of contaminated groundwater. Rather, groundwater contaminated with CAHs flows through granular, zero-valent iron in a trench, which is excavated perpendicular to the axis of groundwater flow (Figure 1). Other metals (e.g., zinc, tin, and palladium) have also been shown to be effective in the degradation of CAHs, but are more costly and potentially toxic.⁵ The volume of groundwater captured and treated can be controlled by using sheet piling "funnel walls" to direct water into the reactive media. This is often referred to as the funnel and gate method. Dissolved CAHs are degraded through a series of less highly chlorinated intermediates^{6,7} to the nonchlorinated saturated and unsaturated analogs. For this demonstration, a reactive wall consisting of a 10-foot wide permeable iron gate flanked on each side by 15-feet long impermeable sheet piling "funnel walls," was installed to a depth of 18 feet below ground surface (bgs) (Figure 2).

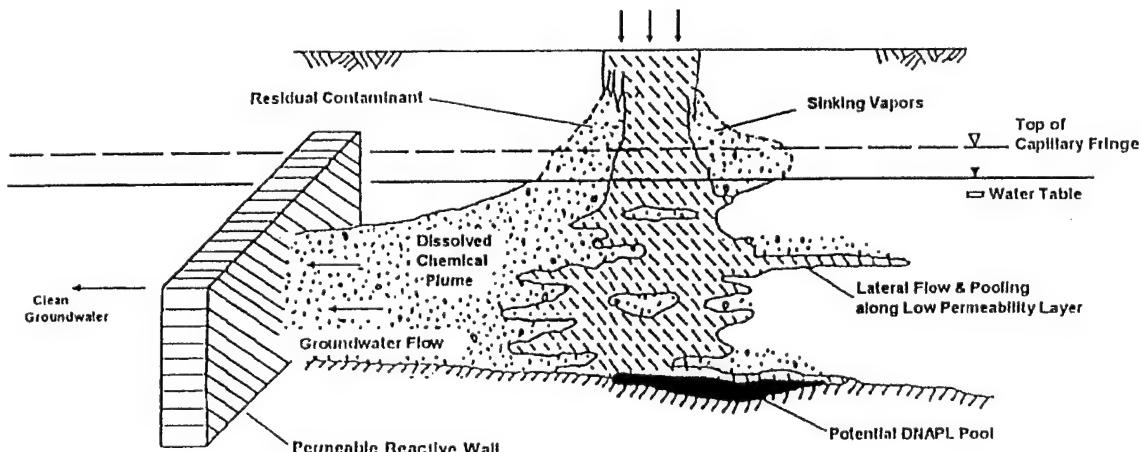


Figure 1. Permeable Reactive Walls (Passive, *In Situ*)

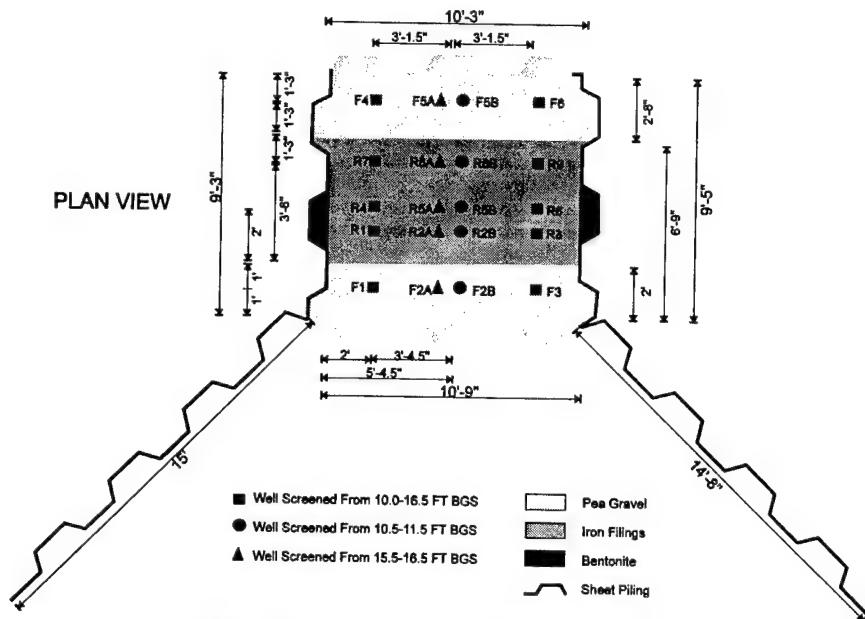


Figure 2. As-Built Treatment Wall Dimensions, Material Composition, and Monitoring Well Locations

In situ zero-valent iron reactive walls have been installed previously and are described in the literature at Canadian Forces Base Borden⁸ and at a commercial electronics manufacturing site in Sunnyvale, California.^{9,10} The Canadian site has the longest operating history of any known site and is reported to have performed without significant change for several years. CAHs present in the groundwater (TCE and perchloroethylene [PCE]) at the site were effectively reduced in concentration after passing through the reactive wall. The commercial electronics site has been in operation for less time and operating results have not been published.

2.1.1 Site Requirements

For the purposes of this demonstration, a major site-selection criterion was the presence of dissolved-phase CAHs at concentrations in excess of 100,000 µg/L. These concentrations approximate worst-case conditions for calculating degradation rate constants over a broad range of concentrations. However, site topography, the potential presence of dense, nonaqueous phase liquid (DNAPL), and an adjacent stream precluded installing the reactive wall in the area with highest concentrations of CAHs. Thus, the reactive wall was installed in an area where CAH concentrations were lower (approximately 1,000 µg/L) but still significant.

Another requirement was a relatively shallow depth of contamination (less than 30 feet bgs). This reflects depth limitations of the installation techniques planned for use at Lowry AFB. Also, the funnel and gate method is benefited by a confining layer, which prevents contaminated groundwater from flowing under the reactive wall, thus escaping remediation.

2.1.2 Possible Chemical Mechanisms

The successful application of this technology may be dependent on site-specific conditions, which effect the chemical mechanism of the degradation pathway. For example, the buffering capacity of the groundwater may affect reaction rates through the neutralization (or absence) of OH⁻¹ produced by oxidation of zero-valent iron with concomitant effects on groundwater pH. Thus, an understanding of the

chemical reaction mechanism is important for the proper evaluation of a prospective site's suitability for remediation by this technology.

Data from a bench-scale column test using groundwater from the Lowry AFB site, as well as other bench-scale studies, suggests three possible mechanisms for the reductive dechlorination of CAHs using zero-valent iron—(a) oxidation of Fe^0 to Fe^{+2} , followed by reduction of CAHs by the Fe^{+2} produced; (b) catalytic reduction of CAHs at the metal surface by the H_2 produced from oxidation of Fe^0 to Fe^{+2} ; and (c) direct reduction of CAHs at the metal surface involving the oxidation of Fe^0 to Fe^{+2} with direct transfer of electrons (Figure 3). Matheson and Tratynek¹¹ and Gillham and O'Hannesin¹² provide a discussion of these mechanisms.

The cell potentials indicated in Figure 3 for individual half cells of each mechanism implies that a significantly reducing environment, as reflected in a negative-redox potential, should be created if any of these mechanisms is operable. The first two mechanisms postulated, reduction by Fe^{+2} and catalytic reduction by H_2 , imply that increases in OH^- concentration could inhibit the reductive dechlorination. The above parameters were studied, and this paper reports data concerning potential mechanisms.

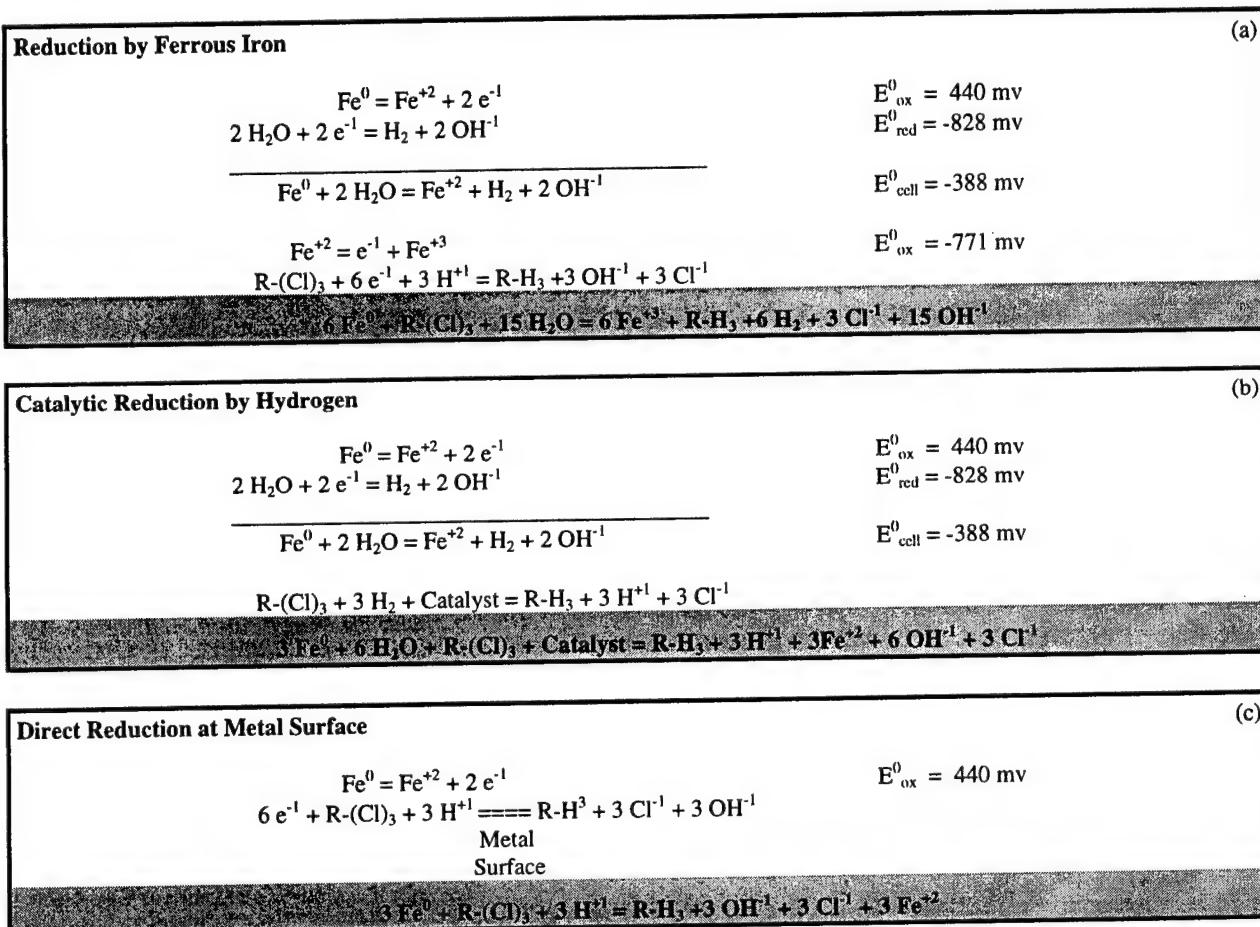


Figure 3. Suggested Chemical Mechanisms for the Reductive Dechlorination of Dissolved-Phase CAHs in the Presence of Iron. (Stoichiometrically Balanced Equations for Degradation of TCE by Each Mechanism are Contained in the Shaded Box.)

2.2 Objectives of the Study

The overall purpose for demonstrating this technology was to assess its usability in similar circumstances at other Air Force installations. The following objectives were identified to support the assessment and implementation of the study:

- Demonstrate effective mass reduction of dissolved CAHs at a lower cost than alternatives, such as pump and treat strategies. Although cost effectiveness is critical to widespread applications, it must be realized that a reactive treatment wall will, if designed properly, degrade toxic CAHs to below quantitation limits, while pump and treat approaches merely transfer CAHs from one media to another and do not eliminate the need for additional effort (i.e., disposal of contaminated carbon or treatment of air stripper vapor-phase effluent).
- Determine first order degradation rate constants. Reliable rate constants are necessary for the design of future cost-effective treatment walls.
- Evaluate precipitation of salts within the wall. Iron (or other) salts could degrade the effectiveness of the wall by impairing groundwater flow, resulting in a reduction of mass CAHs treated or discharge of contaminated groundwater.
- Evaluate end-products produced by reductive dechlorination. A corollary to effective reduction of CAH mass is the production of relatively innocuous by-products. For example, should dechlorination only proceed to the vinyl chloride stage, the solution could be more hazardous than the problem.
- Obtain data to elucidate the mechanism operating to degrade CAHs within the reactive wall.

3. FIELD DEMONSTRATION

The field demonstration was designed to accomplish the aforementioned overall approach and supporting objectives. The field demonstration involved four steps—location characterization, design, construction, and evaluation.

3.1 Location Characterization

The location of the reactive wall was chosen as described in Section 2.1.1, and a site characterization effort was conducted to determine engineering/design parameters for the wall. This effort involved the evaluation of existing regional-scale information; the installation of soil borings and monitoring wells; and provided information on the spatial distribution of hydraulic conductivity, hydraulic potential, excavability, penetrability, and chemistry at the reactive wall location.

The distribution of hydraulic conductivity appeared to be heterogeneous, as evidenced by interbedded sands, silts, and clays observed in the borehole core collected from the alluvial aquifer. Groundwater flow rates across the chosen location were estimated to be approximately 1 foot/day, based on geometric means of existing pump-test data and measured potentiometric gradients. A low permeability claystone (bedrock) underlays the alluvial aquifer at a depth of approximately 17.5 feet bgs. The depth to water was approximately 8 feet bgs at the wall location. The DNAPL source is believed to be located 300 feet upgradient (south) of the wall location.

3.2 Design Approach

The foregoing information was used to determine the design parameters for the reactive wall. Hydraulic conductivity and potentiometric information were numerically modeled to simulate the effects of various wall design scenarios. This iterative process revealed that the design shown in Figure 2 would optimally funnel groundwater through a treatment gate (reactive wall), while avoiding impacts to groundwater or surface water at a nearby stream. Groundwater flow velocities through a gate of this design were predicted to be approximately 2.60 feet/day. This flow rate was used to determine (in part) the thickness of the reactive wall parallel to groundwater flow that would result in the residence time necessary to degrade CAHs to below target concentrations. The required residence time was also determined from degradation rates derived from laboratory column tests conducted on groundwater from the site. This information was also used to design the performance monitoring scheme for the reactive wall. See Figure 2 for the location of the monitoring wells.

3.3 Construction Approach

The construction of the reactive wall involved the use of sealable sheet piling (Waterloo Barrier) driven approximately 18 feet bgs with a crane-mounted hydraulic vibratory hammer. The sheet piling penetrated approximately 6 inches into the low-permeability claystone bedrock. The sheet piling was installed to form a box-shaped gate (reactive wall) with two funnel walls attached. Native material was excavated from the wall using a crane-mounted clamshell; engineered supports were installed to maintain structural integrity of the gate. After excavation, the reactive media (zero-valent granular iron) and various groundwater flow control media (bentonite and 3/8-inch gravel) were emplaced within the wall as shown in Figure 2. Then the sheet piling on the upgradient and downgradient sides of the wall (i.e., gate) were removed to allow groundwater to funnel into and through the reactive iron. Thirty-seven wells and five stream gauges were installed within and around the wall to monitor remedial performance and the influence on surrounding groundwater and surface water flow patterns.

3.4 Evaluation Approach

The performance results of the reactive wall were obtained during the first four months of operation, including a time-zero data point (early December 1995). Performance monitoring involves potentiometric, as well as chemical monitoring. Potentiometric monitoring provided information regarding groundwater flow patterns and variations in these patterns over time. To date, the potentiometric data indicate that flow patterns have been stable and consistent with the numerical modeling predictions.

Chemical monitoring involves the collection and analysis of groundwater samples from the wells shown in Figure 2 and 3 upgradient and 3 downgradient wells not shown in the figure. These wells outside of the wall were screened throughout the saturated zone. All groundwater samples were analyzed for CAHs by Methods SW8010 or SW8260, cations by Method SW6010, anions by Method E300, and field parameters discussed in Section 4. The latter measurements (except alkalinity) were made using a closed-system flow-through cell. Samples for inorganic analyses were obtained using peristaltic pumps with dedicated sampling tubing. Samples for organic analyses were collected using dedicated bailers.

4. RESULTS AND DISCUSSION

4.1 Performance

Concentrations of CAHs were measured in samples taken monthly from the following monitoring wells: upgradient (0 feet); R1, R2, and R3 (1 foot); R3, R4, and R5 (2 feet); and R6, R7, and R8 (3.5 feet). Performance, as measured by the extent of degradation of individual CAHs, was 100 percent in every case and during every sampling event.

4.1.1 Concentration Data

Numerous degradation products of TCE and PCE were present in the groundwater, implying the operation of a dechlorination mechanism *in situ*. TCE was the major component detected during each sampling event, followed by cis-1,2-dichloroethene (DCE). Other CAHs were present at concentrations an order of magnitude lower than TCE and DCE. Table 1 presents concentration data averaged over the first four months of sampling, grouped on the basis of reactive wall cross-sectional distance (i.e., distance from upgradient boundary of wall to sampling point) from which residence times were determined. Figure 4 graphically depicts these data.

TABLE 1. AVERAGE CHLORINATED ALIPHATIC HYDROCARBON CONCENTRATIONS

Wall Cross Section (feet)	TCE	cis-1,2-DCE	trans-1,2-DCE	Vinyl Chloride	1,1-DCE	1,1,1-TCA	PCE	1,1-DCA	1,2-DCA
0	848	221	15.6	24.2	16.3	16.8	13.6	6.56	6.02
1	1.05	10.2	0.23	0.72	0.25	0.17	0.28	0.89	0.49
2	0.18	0.77	0.12	0.47	0.10	0.10	0.25	0.16	0.25
3.5	0.10	0.20	0.10	0.47	0.10	0.10	0.25	0.15	0.25

Note 1: Individual values are averages of monthly averages

Note 2: Non-detect results quantitatively entered as one-half respective quantitation limit

Table 1 indicates that degradation was substantially complete by the time groundwater had flowed 1 foot into the wall (approximately 9 hours residence time). Only cis-1,2-DCE was present at significant concentrations after approximately 9 hours of residence time. By approximately 18 hours of residence time (2 feet into the wall) all analytes had degraded to approximately their respective analytical quantitation limits. The slopes of the concentration curves in Figure 4 are proportional to the first order rate constants. The slowest rates of degradation are for cis-1,2-DCE, 1,1-dichloroethane (DCA), and 1,2-DCA. The results for cis-1,2-DCE, relative to other CAHs, are consistent with the data presented by Gillham.¹³

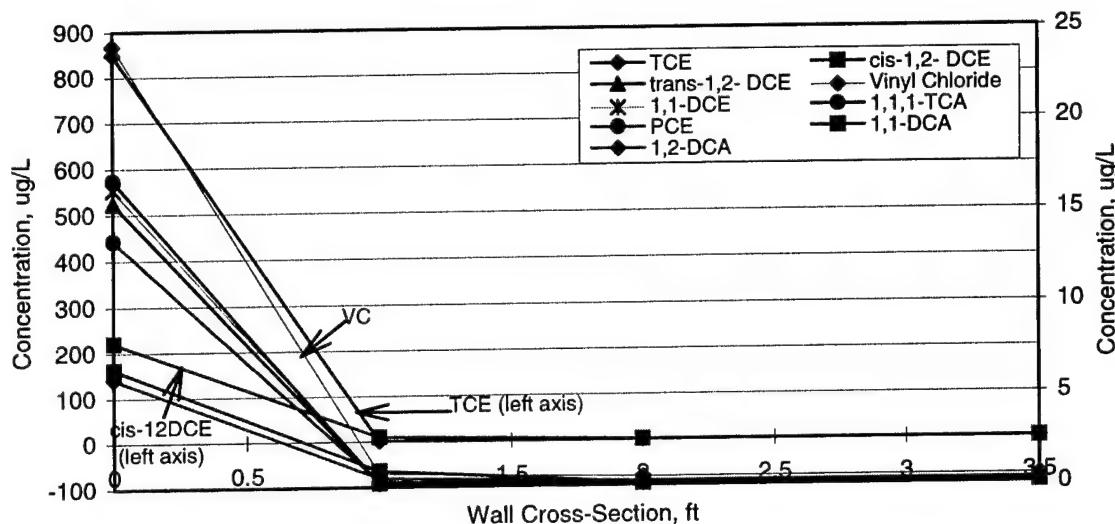


Figure 4. Average (Monthly) Concentrations of Chlorinated Aliphatic Hydrocarbons. Concentrations of TCE and cis-1,2-DCE are on the left axis. Concentrations of all other CAHs are on the right axis.

4.1.2 Calculated Rate Constants

First order rate constants for each CAH were calculated using as C_0 the respective upgradient (0 feet cross section) concentration. Only concentrations determined from samples taken at the 1-foot cross-sectional distance were used for the C_t concentrations because CAH concentrations in samples taken at greater distances were typically at the detection limit. Reaction time ("t" in the first order rate equation) was estimated by converting the distance (into the wall cross section) to time at a groundwater flow rate of 2.60 feet/day. The resulting rate constants are shown in Table 2. These rate constants (except for TCE and PCE) are conservative because the C_0 values are based on concentrations of CAHs present in upgradient groundwater and do not reflect the additional amounts produced in the wall by reductive dechlorination. Therefore, the actual maximum concentrations existing within the first 1 foot of the wall are unknown (except for TCE and PCE) and may be considerably higher than the upgradient concentrations used as C_0 . When the C_t concentrations are near the quantitation limit, the actual time required to reach that concentration may not be the "t" determined to the first sampling point. Overestimating "t" would result in underestimating the rate constant.

The monthly average rate constants are based on the concentrations averaged over the three wells present at each wall cross section (i.e., R1, R2, and R3 for the C_t concentrations). The standard deviations imply that the rate constants and the reductive dechlorination mechanism are not varying significantly over time. The consistency of the rate constants implies that the reactive wall reached chemical equilibrium rapidly. Data presented subsequently reinforces this conclusion. The half lives presented in the table will be useful for designing future reactive walls using 100 percent zero-valent iron.

TABLE 2. AVERAGE¹ FIRST ORDER DEGRADATION RATE CONSTANTS (K, DAY⁻¹)

Sampling Month	TCE	Cis-1,2-DCE	Trans-1,2-DCE	Vinyl Chloride	1,1-DCE	1,1,1-TCA	PCE	1,1-DCA	1,2-DCA
January	16.7	7.94	9.49	10.3	10.5	10.9	8.37	5.04	8.37
February	18.2	8.15	11.9	8.74	10.4	12.9	10.8	5.19	5.43
March	17.7	7.95	12.7	6.98	12.6	13.2	10.8	5.36	5.52
April	17.4	6.91	10.4	6.36	10.5	12.5	10.7	4.75	4.60
Average of Observations	17.5	7.74	11.1	8.08	11.0	12.4	10.2	5.08	5.98
Standard Deviation of "k"	0.61	0.56	1.44	1.76	1.05	1.03	1.20	0.26	1.65
Calc Half Life, Hr	0.9	2.2	1.5	2.1	1.5	1.3	1.6	3.3	2.8
Note 1: Calculated from average of monthly average concentrations									

4.1.3 Degradation End Products

The implication of any of the mechanisms suggested in Figure 3 is the production of less highly chlorinated and more highly saturated hydrocarbons. Evidence of degradation should be accompanied by the appearance of reductive dechlorination end products. Figure 5 illustrates the concentrations of methane, ethane, and ethene in groundwater obtained from one round of sampling (March). Concentrations of ethane and ethene, the proposed end products, reached a maximum at a wall cross-sectional distance of 1 foot. The peak concentrations correlate with the peak CAH degradation activity within the wall, as illustrated in Figure 4. Beyond the 1-foot distance, concentrations of all three gases decrease, indicating a reduction or cessation of their production.

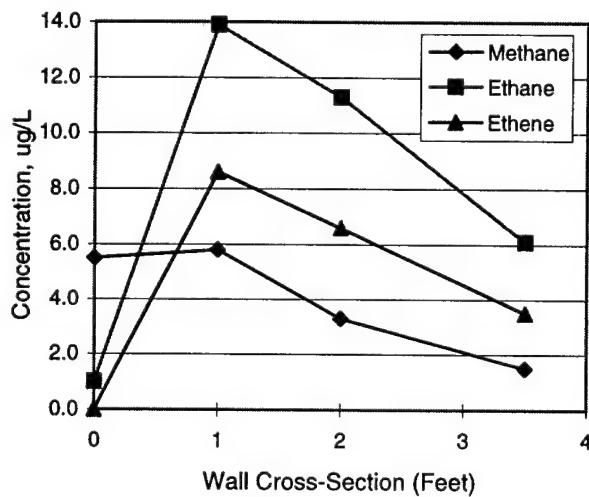


Figure 5. Methane-Ethane-Ethene
Concentrations in Groundwater as Function
of Cross-Sectional Distance of Wall

Note that methane and a small amount of ethane were present in the upgradient groundwater. This, in addition to the presence of CAH degradation products upgradient from the reactive wall, may indicate that reductive dechlorination occurs within the native aquifer and that methanogenesis is occurring, either as part of or in addition to the degradation. However, reduction of aqueous CO₂ by iron in the aquifer, which can form hydrocarbons, can not be conclusively eliminated as the source of these hydrocarbons.¹⁴

The presence of ethane and ethene may indicate that the reduction of saturated and unsaturated CAHs occurs in parallel (i.e., saturated CAHs go to ethane and unsaturated CAHs go to ethene) or that ethane is the final product of reduction and possibly accumulates in the aquifer.

4.2 Evidence for Mechanism

Based on the mechanisms suggested in Figure 3, the presence of Fe^{+2} , Fe^{+3} , OH^{-1} , and a reducing redox potential might be used to elucidate the mechanism operating for the reductive dechlorination of CAHs. The redox potential of the groundwater flowing through the reactive wall rapidly becomes strongly negative, as illustrated in Figure 6, and presumably reflects the oxidation of Fe^0 to Fe^{+2} . Redox potential results for January are anomalous in light of the degradation already occurring, but subsequent measurements are consistent with the oxidation of iron. However, it is possible that this oxidation is occurring in addition to another degradation mechanism, and these redox potentials do not clearly imply one or another mechanism.

Similarly, the groundwater pH results in Figure 7 seem to reflect the production of OH^{-1} , which is possible by each mechanism in Figure 3, although mechanism "c" (direct reduction at metal surface) does not appear capable of producing sufficient amounts of OH^{-1} to cause such a large elevation of pH. Discussion of alkalinity changes supports the notion that a relatively large quantity of OH^{-1} was produced, thus these data are supportive of mechanisms "a" and "b" and would seem to rule out mechanism "c."

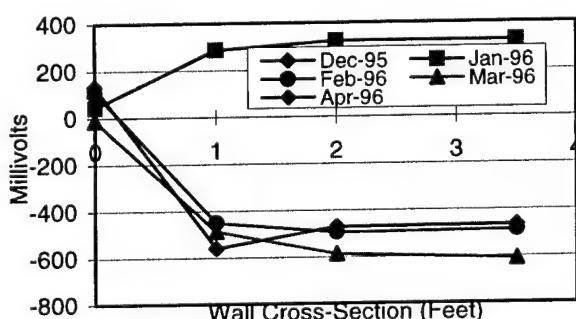


Figure 6. Redox Potential in Groundwater as Function of Wall Cross-Sectional Distance;
Dec 95 = 94 mv

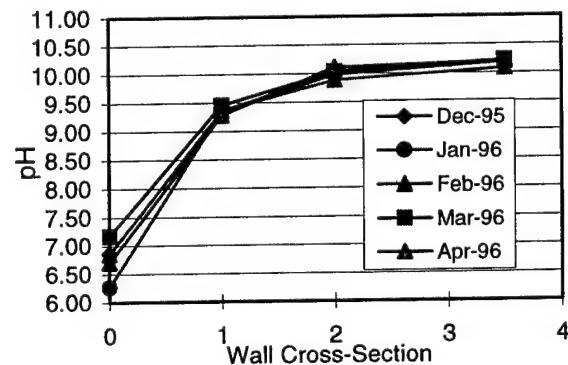


Figure 7. Groundwater pH as Function of Wall Cross-Sectional Distance;
Dec 95 pH = 6.86

4.3 Precipitation

Precipitation has been shown to occur (pilot study results) as a result of the insolubility of certain iron salts at the pH and redox potential existing in the reactive wall. Total alkalinity decreased rapidly with cross-sectional distance into the wall during every sampling event (Figure 8). The total alkalinity upgrade of the reactive wall exists as bicarbonate (HCO_3^{-1}), as expected for groundwater with a near-neutral pH (Figure 9). Bicarbonate concentrations rapidly decline as a function of wall cross section, due to the increasing groundwater pH which shifts the CO_2 equilibrium from the HCO_3^{-1} species to carbonate (CO_3^{-2}). However, CO_3^{-2} is rapidly lost, as illustrated in Figure 10, presumably due to its precipitation as FeCO_3 and possibly $\text{Fe}_2(\text{CO}_3)_3$. This corresponds to approximately 5.9 mmoles/L of CO_3^{-1} species lost, which means that a total of approximately 6.2 mmoles/L (105 mg/L) of OH^{-1} were produced, most of which neutralized HCO_3^{-1} and very little of which remained to contribute to the Total Alkalinity.

downgradient of the 1-foot wall cross section (Figure 11). As previously mentioned, it is difficult to reconcile this quantity of OH^- being produced by mechanism "c" (Figure 3). In addition, both calcium ion and sulfate ion concentrations in groundwater were significantly reduced as groundwater encountered the highly reducing and alkaline conditions within the reactive wall, adding to the precipitation occurring within the wall.

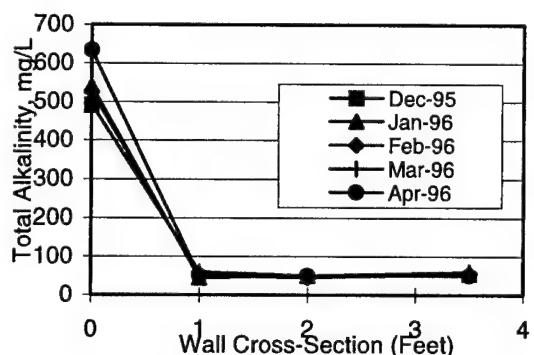


Figure 8. Groundwater Total Alkalinity as Function of Wall Cross-Sectional Distance; Dec 95 = 490 mg/L

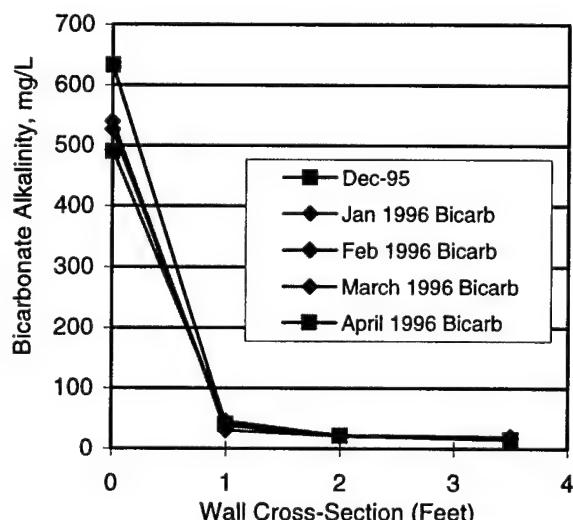


Figure 9. Groundwater Bicarbonate Alkalinity as Function of Wall Cross-Sectional Distance
Dec 95 = 490 mg/L

The presence of Fe^{+3} would imply that reductive dechlorination occurs by oxidation of Fe^{+2} in solution to Fe^{+3} . Due to the precipitation of iron salts, Fe^{+2} and Fe^{+3} were not detected at concentrations greater than 1 mg/L.

5. COST EVALUATION

An integral part of this study is to evaluate and compare the costs of remediation using this technology with other remedial techniques. The cost of this demonstration was high because of the conservative overdesign of the wall and the intensive sampling and analysis program needed to evaluate the

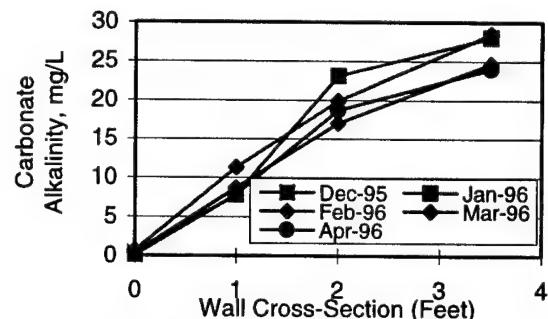


Figure 10. Groundwater Carbonate Alkalinity as Function of Wall Cross-Sectional Distance; Dec 95 = 0

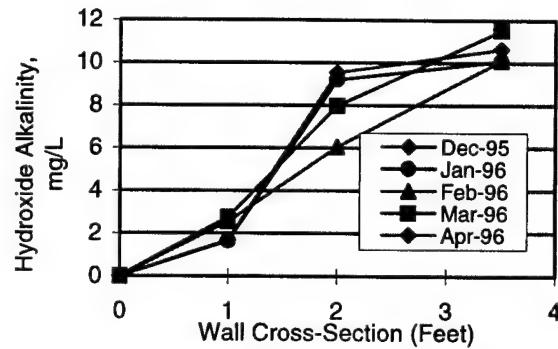


Figure 11. Groundwater Hydroxide Alkalinity as Function of Wall Cross-Sectional Distance; Dec 95 = 0

performance. Using this technology routinely, will not require such intensive sampling or analysis, lowering costs compared to the demonstration reported in Figure 12.

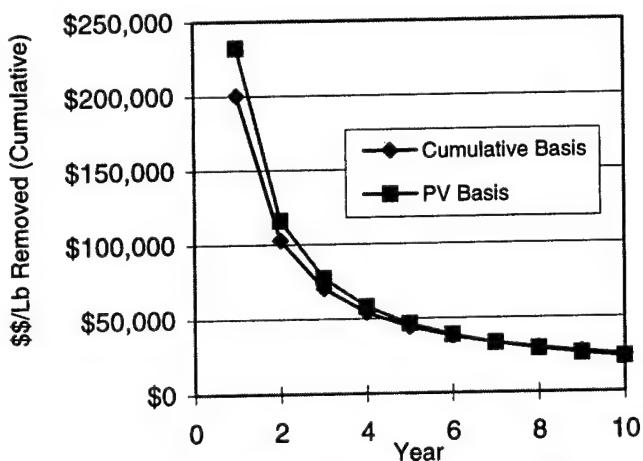


Figure 12. Average Treatment Cost

Figure 12 illustrates the cost per pound of CAH removed for a 10-year time horizon. It was assumed that concentrations and degradation rates and analytical costs are constant over time. It also was assumed that iron replacement was not required during this period. Costs were determined as both the present value and cumulative current costs. Because most of the cost is incurred early (i.e., for installation), the present value and cumulative current costs do not differ very much. The cost of this method approaches \$24,000 per pound of CAH removed (Figure 12). This cost can be expected to be significantly lower as design criteria are further refined for full-scale remediation.

6. CONCLUSIONS

The evidence presented indicates that the zero-valent iron reactive wall is actively degrading CAHs dissolved in groundwater. Degradation is complete and relatively rapid and results in the formation of both ethane and ethene as possible end-products of the degradation. First order rate constants were calculated based on the known upgradient concentrations for each CAH detected. These rate constants are probably conservative in that they may not represent the highest (C_0) concentration of the individual compound, and the actual time for complete degradation of many CAHs is only estimated (based on the time required for groundwater to travel to the monitoring well).

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AUTOMATED TRACE METALS ANALYZER

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ABSTRACT

Metal contamination arises from many sources and does not biodegrade in the environment. Prevention of soil and sediment contamination can only be accomplished by effective real or near-real-time monitoring of effluents, process streams, and runoff.

Field measurement of metals is difficult due to the size and complexity of the standard analytical instrumentation. Current laboratory methods employ either atomic absorption spectroscopy or inductively coupled plasma spectroscopy. Although these instruments are capable of low parts per billion measurements, they are expensive, sensitive to matrix affects, and require experienced operators as well as significant infrastructure support for field use. These systems are also not well suited for continuous automated monitoring of effluent and process streams.

A prototype automated trace metals analyzer has been developed based on the electrochemical technique of potentiometric stripping analysis. This technique was pioneered by D. Jagner in the early 70's. Recent advances in electronics now enable this technique to perform a completely automated metal analyses to less than one part per billion in about three minutes. The instrument, weighing less than 10 kg, provides a capability to perform on-site, discrete analyses, or continuous, automatic monitoring at programmed intervals over extended periods. The analyzer can be packaged in many configurations to suit specific requirements. These include minimum size for maximum portability, NEMA enclosures for industrial locations, or bench top systems for laboratory settings.

1. INTRODUCTION

In industrial process control and environmental compliance monitoring graphite furnace atomic absorption (AA) spectroscopy and inductively coupled plasma mass spectroscopy have been traditionally used to measure trace metals. These instruments are large, expensive, and require a high level of infrastructure support. Because of this, trace metal measurement usually involves sampling, preservation, and transport to a centralized laboratory for later analysis. Current field tests for metals are difficult to use under field and industrial conditions, usually lack simultaneous multianalyte capability, and require operator intervention. The Automated Trace Metals Analyzer (ATMA) overcomes most of these problems. This instrument is capable of automated multianalyte trace metal analysis in the field using potentiometric stripping analysis (PSA). This technique is capable of measuring over 40 metals with enough sensitivity to detect concentrations in the low parts per billion range¹. It has been used to detect metals in diverse fluids such as drinking water², wine³, sediment⁴, and blood⁵.

The windows based interface enable nontechnical personnel to setup the instrument and collect data with minimal training. The instrument continually monitors performance and will automatically notify the

operator and log any problems that it can not correct. While in operation the instrument is sealed from the external environment excluding the possibility of sample contamination.

2. PRINCIPLE OF OPERATION

The two step PSA process was originally developed by Jagner⁶. In the first step metals in the sample solution are reduced by applying a negative potential to the working electrode in a process similar to that occurring in a plating bath. This step concentrates the metals and typically requires about 30 seconds depending on the amount of metals in solution. The second step involves applying a constant current to the working electrode or removing the voltage potential from the working electrode while measuring the potential as a function of time. As the potential falls, each metal is oxidized at a specific voltage. During the metal oxidation the potential remains constant resulting in a plateau in the potential versus time plot (Figure 1.). The length of the plateau is proportional to the amount of metal originally in solution. To calculate the true concentration of the metal a standard curve is generated by adding known quantities of the metals of interest to the test sample and repeating the measurement. This entire process is totally automated and proceeds without any intervention. When the concentrations of the metals have been determined (usually in less than 3 minutes) the instrument displays and logs the concentrations and the relevant measurement statistics, pumps out the test sample, rinses the cell, and waits for either an operator command or the next programmed sampling interval.

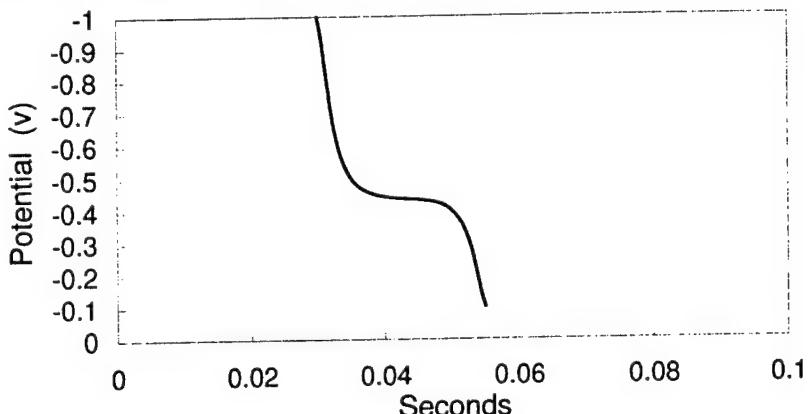


Figure 1. Potential of the reference electrode over time after the reducing voltage is removed. The potential falls until it reaches a value where a specific metal will be oxidized, in this case lead. The potential remains constant until all of the metal is oxidized. This plateau is proportional to the original concentration of metal in the solution. Each metal has a characteristic voltage at which it is oxidized enabling multiple metals to be measured simultaneously.

3. SYSTEM DESCRIPTION AND PERFORMANCE

The ATMA consists of two main components. The first component consists of a computer containing custom software and hardware used to control the electrochemical cell operations, data acquisition, and data analysis. The second component is the mechanical package holding the pumps, reagents, and test cell. The test cell contains a removable reference, counter, and working electrode. Injection ports are located radially around the cell which has a sample volume of 2.5 mL. The entire unit weighs less than 10 kg and can be transported in two cases which will fit under an airline seat. The ATMA is capable of running unattended for up to ten days. The auto-sampling rate is adjustable up to a maximum of one sample per minute. The instrument can also be run manually for discrete

measurements under operator control or it can be triggered by an external signal from a user provided sensor.

A comparison of graphite furnace AA and ATMA results for lead levels in drinking water are shown in Figure 2. The samples were collected, split, and analyzed simultaneously with the AA and ATMA. The correlation coefficient (R^2) is 0.94 with a slope of 0.95 indicating agreement within experimental error between the two instruments.

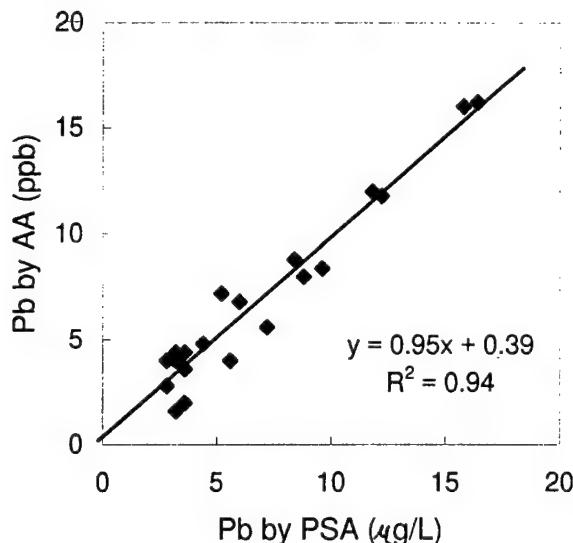


Figure 2. A comparison of graphite furnace AA and ATMA results for lead levels in drinking water. Each point is a single drinking water sample, the X axis is the level measured by the ATMA the Y axis is the value measured by the AA.

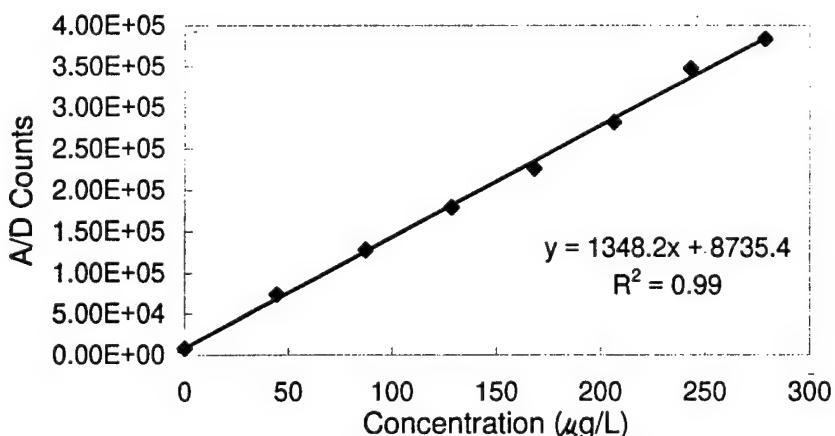


Figure 3. Linearity of the ATMA for lead concentrations between 0 and 300 µg/L. A/D counts is the number of samples the instrument's A/D converter measured while the electrode potential was at the characteristic stripping potential for oxidizing lead.

The linearity of the ATMA over a range of 0 to 300 µg/L lead is shown in Figure 3. An eight point standard addition test was conducted using a single sample of double distilled water spiked up to a level of 280 µg/L. On the Y axis A/D counts is the number of samples the analog to digital converter

measured which were at the characteristic potential for oxidizing lead. This is a direct measurement of the length of the plateau shown in Figure 1. A correlation coefficient of greater than 0.99 was obtained indicating excellent linearity within this range.

4.CONCLUSIONS

The ATMA is useful in many situations where there is a need to know, with single parts per billion accuracy, the concentration of heavy metals in the field and in industrial process control. Because the instrument can be brought to the site for measurements the risk of sample contamination is much lower than with conventional on-site sample preservation and transport, in addition the automated capabilities allow completely unattended operation triggered at timed intervals or external events. Demonstrations under the Environmental Security Technology Certification Program have shown that the per sample cost is less than half that of conventional technology. This easy to use instrument with it's windows based operating system is a viable alternative to the expensive and complex laboratory equipment currently in use today.

5.ACKNOWLEDGMENTS

The authors wish to thank Joseph Wang and Alberto Zirino for their support, and suggestions during the development of this instrument. Demonstration and validation of the ATMA is currently funded by the Environmental Security Technology Certification Program

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THE HOWS AND WHYS OF LANDFILL ENTOMBMENT

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ABSTRACT

Investigations at Robins Air Force Base in Georgia identified an existing closed hazardous landfill as the source for active seeps of contamination into a stormwater channel. The landfill, closed in the mid-1960's, was used for general refuse disposal, laboratory chemical disposal, and fire protection training. Volatile organics, semi-volatile organics, pesticides and priority pollutant metals had high concentrations in soils and groundwater samples. Ground-penetrating radar was used to establish landfill boundaries since limited historical records were available. Soil borings confirmed underlying low permeability clay layers and high permeability sand lenses.

The unknown composition of the refuse, high concentrations of pollutants, environmental hazards and costs associated with removal led to the selection of complete encapsulation (entombment) of the landfill. Design of the entombment included a perimeter soil-bentonite cutoff wall, a two component barrier with a multi-layered cap, and leachate and methane gas collection. The underlying clay layer has a low laboratory permeability, below 1×10^{-7} cm/sec. The two component barrier consists of a bentonite mat and HDPE flexible membrane liner. This system was selected from alternative barrier designs for use as the low permeability infiltration barrier to meet RCRA requirements which state that the cap permeability must be less than or equal to the underlying soil. Long-term permeability and compatibility testing of bentonite mixtures for the cutoff wall with landfill leachate resulted in poor performance of certain bentonites. This led to selection of a sole source bentonite mixture. With entombment, leachate generation is expected to be minimal. However, leachate collection wells are provided to maintain an inward groundwater gradient within the cutoff wall and provide a way to measure excess infiltration from a cover breach or failure. Active gas collection is provided using perforated HDPE piping and a flare for off-gas control.

During construction, numerous problems occurred as a result of starting an aggressive construction schedule in the winter season. A slough of the slurry trench side wall caused concerns about sand lenses affecting the ability of the slurry to hold up the walls of the excavation. Due to the hydrogeological influence of an adjacent recreation lake and upgradient groundwater recharge area, a partial cutoff wall

("horseshoe") was used during soil preloading for preconsolidation of landfill wastes. This approach isolated the landfill hydrogeologically, allowing excess pore pressure caused by preloading to dissipate, minimizing risk of contaminant movement toward the lake and recharge area. Finally, problems with availability of the barrier layer material caused a switch in the liner material from Very Low Density Polyethylene (VLDPE) to High Density Polyethylene (HDPE). Material testing was critical since it uncovered deficiencies in the HDPE failing to meet industry standards.

The Air Force, in an attempt to save costs, suggested changes to the design which eliminated a gravel layer used for methane gas collection and in its place installing French drains. A geocomposite drainage layer was substituted for a 12-inch sand drainage layer. Subsurface drainage (above the barrier layer) was diverted to eliminate a gravity pipe system. Construction is nearly complete, and recent groundwater sampling results indicate successful achievement of objectives.

1. INTRODUCTION

The Warner Robins Air Logistics Center, located at Robins Air Force Base, Georgia, has conducted a series of investigations under the Installation Restoration Program (IRP). The purpose of the IRP is to identify and remediate sites on military installations that may have been contaminated during historical operations. Three sites were grouped together for investigative and remediation purposes and are further described as follows.

- Landfill No. 3 is a four acre area located immediately west of Luna Lake on the Base that received approximately 65,000 cubic yards of general refuse during its one year operation in 1964.
- Located within the boundaries of Landfill No. 3 is a second source of contamination, the Laboratory Chemical Disposal Area. This site reportedly consists of two unlined pits that were used for a one-time disposal of small jars and bottles of laboratory chemicals that had exceeded their recommended shelf life.
- The third source is Fire Protection Training Area No. 2 consisting of several open-burn sites using various flammable chemicals. These burn sites were located west and northwest of Luna Lake.

Subsequent site investigations of Landfill No. 3 employed groundwater wells, soil borings, electromagnetic conductivity surveys, electrical resistivity surveys, test pit excavations, and ground penetrating radar. These investigative techniques were used to determine the boundaries of each of the three disposal sites and identify the types and concentrations of the contaminants present. They indicated that the three individual sites are contiguously located in an area approximately six acres in size, immediately adjacent to the west shore of Luna Lake.

Analytical testing of soil and groundwater samples taken from the site indicate the presence of volatile organics, semi-volatile organics, heavy metals, and pesticides. The volatile organics present include dichloroethane, trichloroethane, chlorobenzene, toluene and xylene. The semi-volatiles discovered include dichlorobenzenes and dimethylphenols. Heavy metals determined to be present in concentrations higher than the maximum contaminant levels (MCLs) for drinking water include cadmium, chromium, and lead, with the pesticides DDE and DDT also present.

The Air Force has proposed a series of remedial actions to isolate and contain the site's contamination and prevent further migration to soil, surface water, and groundwater resources. These remedial actions include the construction of a sub-surface soil-bentonite cutoff wall, a multi-layer impermeable landfill cover, a leachate collection system, a methane gas collection and treatment system, and a groundwater dewatering system. These remedies are necessary for source containment. An integral part of source containment is the continued maintenance of an inward groundwater gradient across the slurry cutoff wall and maintenance of the final cover integrity.

2. PURPOSE AND NEED FOR PROPOSED ACTION

The purpose of the proposed action is to completely isolate and contain contaminants found in Landfill No. 3 and prevent migration into the underlying Providence and Blufftown aquifers. The Providence aquifer directly overlays (and is hydraulically connected to) the Blufftown aquifer, which serves as the primary drinking water source for the City of Warner Robins. The remedial activities would also eliminate current releases of contaminants into streams and creeks located down gradient from the site.

3. ALTERNATIVES CONSIDERED

Selection of the preferred course of action involves the comparison of alternative solutions on the basis of many factors. A variety of alternatives were considered, including:

- no action,
- removal and off-site disposal of the site's contaminants,
- In-situ treatment, and
- contaminant source isolation and containment (the chosen alternative).

The no action alternative was rejected because it would neither eliminate nor isolate the source of contamination that could eventually migrate to the underlying Providence and Tuscaloosa aquifers. The second alternative, excavation of the site's wastes and transportation to an off-site permitted hazardous waste disposal facility, was rejected for the following three reasons:

3.1 Safety

During excavation of unknown quantities of contaminated materials, site personnel would be exposed to chemical vapors and airborne contaminants. Although exposure can be controlled with personal protective equipment, releases of volatile organic compounds (VOC's) during excavation could reach lower explosive limits. This would create extremely hazardous working conditions and require immediate evacuation of both the site and surrounding area until escaped gases disperse.

3.2 Environmental Releases

Because engineering controls cannot fully prevent or contain VOC's released during excavation, transportation and disposal, quantities of VOC's would be released to the environment during these activities.

3.3 Costs

The cost of transporting and disposing of the wastes at the nearest permitted hazardous waste disposal facility were prohibitively high. Approximately 250,000 cubic yards of soil and landfill wastes would require disposal. The nearest permitted disposal facility is the Chemical Waste Management facility at Emelle, Alabama, approximately 310 miles away. In addition to the short term disposal costs, the Air Force's long-term liability associated with disposing of wastes in a hazardous waste landfill also contributed to the rejection of this alternative.

In-situ methods such as pump and treat or soil treatment were screened from consideration because of high costs and length of time to accomplish objectives. The proposed alternative of source containment was selected because it most effectively met the project criteria and was determined to be preferable to the other alternatives.

4. INTERIM MEASURES

The measures taken during the period between October 1993 and April 1996 are considered interim since immediate treatment of the migration of contaminants was necessary for protection of public health. In general, interim measures are typically expedited immediate response actions. The interim measures at the site precede additional work that is to be described in a Corrective Action Plan.

The interim measures implemented at Landfill No. 3 more specifically include the following features:

- Construction of a soil-bentonite cutoff wall with a permeability less than or equal to 1×10^{-7} cm/sec. Because the underlying soil has a permeability ranging from a high 3×10^{-7} cm/sec to a low 2×10^{-8} cm/sec, the slurry cutoff wall was designed within this range. The slurry cutoff wall, through its low permeability boundary, severs the hydraulic connection between Luna Lake and the landfill, and groundwater inside the landfill with groundwater outside the cutoff wall.
- Construction of a landfill cover composed of common soil fill, bentonite mat barrier, 40 mil High Density Polyethylene (HDPE) barrier, geocomposite drainage layer, engineering geotextile, topsoil, subdrains, and necessary surface grading. The purpose of the cover is to restrict rainfall infiltration from the surface. Environmental Protection Agency guidelines for RCRA sites suggest the permeability of the cover be less than or equal to the underlying soil. Permeability of this cover is expected to be substantially less than that of the underlying soil.
- Construction of a permanent leachate collection system including extraction wells, submersible pumps, double containment pipes, wet well, dry well and controls. Because the effectiveness of the source control requires an inward groundwater gradient through the slurry cutoff wall, leachate removal is needed. Leachate is collected and removed from the site via the leachate extraction system.
- Construction of a landfill gas venting system including screened gravel trenches, HDPE perforated collection pipes, 40 cubic feet per minute (SCFM) positive displacement blower, condensate removal, landfill gas combustion flare, vent stack and controls. This system is to remove and treat methane and other landfill gases that pocket under the landfill cover causing premature degradation of the cover.

- Soil preloading for preconsolidation of the landfill. Preloading was included to mitigate the effects of settlement, and to reduce the uncertainties inherent in estimates of landfill cover integrity after the cover is placed in service.

5. RESULTS OF DESIGN, TESTING AND EVALUATION

5.1 Test Pits

Bulk soil and groundwater samples were collected from three test pits excavated by backhoe along the alignment of the slurry cutoff wall. The samples from each pit were collected for use in bentonite design mix tests and compatibility tests. Samples were tested for target compound list organics, semi-volatiles, pesticides, PCB's and target analyte list metals.

5.2 Compatibility Testing.

A series of tests were conducted to determine the compatibility of bentonite with landfill leachate. The objective was to design a stable bentonite slurry mix for trench wall construction and optimum backfill mix for the cutoff wall. Various sources of bentonite were mixed with contaminated water and soil from the landfill and tested for physical stability, flocculation and long-term permeability. Initial results from the tests showed a strong reaction between the contaminated site water and several of the bentonites tested. However, a proprietary product, "Saline Seal" from American Colloid produced an acceptable slurry with satisfactory long-term permeability, viscosity and no flocculation. Thoroughly mixed site soils with 4% Saline Seal sufficiently yielded permeabilities of less than 1×10^{-7} cm/sec in the laboratory. Design of the field mix was established using 5 to 6% Saline Seal. Since thorough mixing is difficult and expensive to accomplish in the field, the increase in volume of bentonite was necessary to achieve similar field results to laboratory test results.

5.3 Groundwater

Throughout construction of the interim measures, groundwater levels within the confines of the slurry cutoff wall were monitored. Prior to implementation of the interim measures, groundwater in the landfill was hydraulically linked to the flow of water seeping from Luna Lake. After construction of the slurry cutoff wall along the Lake side of the landfill (east side), the hydraulic connection was severed. There was concern that groundwater would rise due to reduction of pore volumes in the soil caused by preconsolidation of the landfill, especially with the cutoff wall installed. Since the groundwater was contaminated, maintaining the water surface level in the landfill below the top of the slurry cutoff wall was required to prevent an uncontrolled release of contaminated liquids onto the ground surface. By partially constructing the cutoff wall (leaving one side open similar to a 'horseshoe'), excess pore pressure caused by soil preloading was expected to dissipate out the open end. However, a slough of the slurry trench side wall during construction caused the horseshoe wall to remain open in an area which limited groundwater movement. Groundwater elevations then became influenced by frequent rains and by recharge from a swampy area south of the landfill. At conclusion of the slurry cutoff wall in May 1994, the groundwater level in the landfill approached within two feet of the top of the cutoff wall and remained there until the cover was completed.

5.4 Landfill Gas Sampling

Five air samples were collected from the landfill gas collection system. The samples were analyzed for volatile organic compounds and for methane. A number of chlorinated volatile compounds, hydrocarbons and freon compounds were detected at significant concentrations in all five samples. The highest concentrations of chlorinated compounds were cis-1,2-dichloroethene and vinyl chloride. Concentrations of cis-1,2-dichloroethene ranged from 2,900 to 780,000 ppbv, and vinyl chloride ranged from 540 to 91,000 ppbv. Methane was detected in significant concentrations ranging from 24,000 to 530,000 ppmv. Gas concentrations represent static, confined conditions.

5.5 HDPE Flexible Membrane Liner

Testing to confirm the characteristics of the flexible membrane liner installed at the site was conducted. Several samples were tested at the point of manufacture and rejected for failure to meet strength and elongation requirements. After testing material from several manufacturers, the material ultimately used for the liner proved to be consistent with the industry standard requirements for 40 mil HDPE.

6. CHANGES MADE DURING DESIGN

As in any construction project, field conditions or economic conditions often influence the implementation of the design, resulting in field modifications. Significant changes that were implemented and their affects on the design are outlined below:

- The flexible membrane liner material was modified. During the course of construction, the cost for VLDPE increased significantly and supplies became unavailable. Substitution of a 40 mil thick HDPE liner for the originally designed 40 mil thick Very Low Density Polyethylene (VLDPE) liner was made.
- The screened gravel layer for the gas collection system was eliminated. Instead of a gravel layer over the surface of the landfill, several smaller collection trenches, filled with No. 57 crushed stone aggregate, and similar to the design of a French drain, were used. This trench system, in lieu of the screened gravel layer, was used primarily to achieve cost savings. The trench collection system, although not as effective as the screened gravel layer, is still an acceptable method for gas collection.
- The 12-inch sand drainage layer above the flexible membrane liner was replaced with a thin geocomposite drainage layer. The advantage of the sand layer over the geocomposite was additional soil moisture storage that could be used to support surface vegetation. Cost savings was a controlling factor in this decision.
- The soil cover above the geocomposite drainage layer was reduced from 24 inches to 15 inches. Due to cost considerations, the grading surface was not brought to the elevations as designed. A disadvantage of this decision is that a healthy stand of vegetation may not survive during dry, hot weather periods. Insufficient retained soil moisture in the cover may not support the growth of desirable vegetation.

- Due to project cost growth, the perimeter subdrainage system was also eliminated. Elimination of this system affects the ability of the geocomposite drainage layer to rapidly remove surface water from above the flexible membrane liner. Over many years, water ponding on the surface of the flexible membrane liner may act to weaken the liner, possibly resulting in a rupture. Without the subdrainage piping, runoff from the drainage composite layer must seep through cover soils to drain off the landfill.

7. EFFECTIVENESS OF THE INTERIM MEASURES

Recent analytical data from groundwater well samples from fall 1994 through spring 1996, represent the first concentration measurements with the slurry cutoff wall in place. Groundwater samples taken from wells located adjacent to (outside) the cutoff wall have exhibited significant decreases in contaminant concentrations. The reductions indicate that the cutoff wall has effectively contained hazardous contaminated groundwater within the landfill and allowed uncontaminated groundwater to begin to purge these locations. Continued monitoring will determine if decreasing trends are likely to continue.

8. CONCLUSIONS

Remedial measures were implemented to control the source of hazardous levels of groundwater contamination at Landfill No. 3, Fire Training Area No. 2 and Laboratory Chemical Disposal Area on Robins Air Force Base, Georgia. Source isolation and containment were selected which includes installation of a slurry cutoff wall, a landfill cover, and leachate and gas collection systems. Interim measures were initiated in October 1993 and completed in April 1995. As of spring 1996, sampling data indicate that concentrations of hazardous substances in the groundwater outside the cutoff wall are reducing. The remedial measures are demonstrating effectiveness in containing the contaminant source and controlling migration of pollutants into the environment. With firm establishment of vegetation and wild flowers on the surface of the landfill, the site has been effectively returned to non-intrusive recreational use.

LIQUID NITROGEN AND WATER JET MILLING OF ENERGETIC MATERIAL PRODUCTION WASTES

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EXECUTIVE SUMMARY

U.S. Army Ammunition Plants (AAPs) and Load, Assemble and Pack (LAP) facilities generate pyrotechnic, explosive and propellant (PEP) production wastes of diverse nature. These production wastes can be in the form of "off-spec" energetic material (EM), EM contaminated with foreign substances, or processing equipment and materials contaminated with EM. At most of the facilities, these heterogeneous wastes are destroyed or mineralized by open burning/open detonation (OB/OD), a practice which is scrutinized and restricted because of environmental contamination concerns.

In recent years several alternative technologies to OB/OD have been identified and developed which can process heterogeneous production wastes to ultimate destruction safely. An eclectic approach to the production waste disposal problem has been used based upon the understanding that no single "clean" technology can replace OB/OD. Controlled incineration (CI), wet air oxidation (WAO), hydrothermal oxidation (HTO) and composting have been evaluated and assessed for applicability and efficacy. Each of these alternative destruction technologies for OB/OD require the energetic materials to be reduced to a size compatible with the feed system of the destructor.

Because EM production wastes at Army ammunition plants (AAPs) can be contaminated with tramp metals, rocks, glass, wood and other extraneous matter, conventional metal bladed grinding or shearing equipment cannot be safely used to effect diminution. Thus the question is, how can we safely cut up contaminated EM production wastes, without the use of metal bladed equipment? One solution is hydromilling.

Hydromills are devices which use high pressure waterjets, operating at up to 385 MPa (55,000 psi), as the cutting tools. During FYs 94 and 95, USACERL engineers in collaboration with engineers at the Lonestar AAP (LSAAP), the Radford AAP (RAAP) and Flow International, Inc. designed, constructed and field tested six different prototypes of high pressure waterjet hydromills for the diminution of energetic materials (EM) and energetic material contaminated wastes (EMCW). The hydromills have been designated the X-Y Table, Cone-Cylinder I, Cone-Cylinder II, Tiered Rotosieves, Cylindrical Rotobasket and Drum Mill. The Drum Mill, the last hydromill to be designed, built, and tested, incorporates the best features of its predecessors and has been selected for continued development and use in FY96 research efforts at LSAAP.

The fundamental effectiveness of high pressure waterjets to cut energetic materials was evaluated early in the research using the X-Y Table hydromill. The X-Y Table is a "batch reactor" which employs a set of three rastering high pressure waterjets. During operation, the jets make multiple perpendicular sets of parallel cuts in the EM, which rests on top of a wire mesh platen or table. Blocks of Composition A5, Composition B, PBX-0280 and TNT, as thick as 6.5cm, were readily and safely cut with 0.18 - 0.25 mm diameter waterjets, operating at 280-385 MPa. Samples of Benite, M900 tracer composition and the two propellants M31A1E1 and NOSIH-AA2 were also readily processed with the X-Y Table hydromill. Because the X-Y Table hydromill needed to be loaded and unloaded by hand, design efforts were redirected towards the development of a mill which would

function as a continuous flow reactor. The Cone-Cylinders and the Tiered Rotosieves each had good design features, and could serve as a continuous flow reactor, but did not function as well as expected. The Cylindrical Rotobasket was another batch reactor with feed limitations, but its excellent cutting performance suggested that an earlier considered concept of a rotating drum mill was viable.

Our prototype Drum Mill, which is currently installed in a test bay at the LSAAP, comprises a modified 55 gallon stainless steel drum, which rotates at 2 rpm about its longitudinal axis while supported on a motor driven, rubber-wheeled drum roller and has an interior waterjet manifold. The drum roller and drum are on an angle-iron frame which is inclined at 15° from the horizontal. In this orientation, the Drum Mill resembles a concrete mixer. The feed end of the drum is above the discharge end, which allows gravity assisted movement of the EM within the drum. A rubber wheel, which rolls along a circumferential track at the base of the drum, at the discharge end, serves as a thrust bearing to keep the freely rotating drum properly positioned on the drum roller. The high pressure water manifold has eleven waterjets, each with a 0.15 mm diameter orifice. The jets are spaced evenly along the 82 cm long manifold. The high pressure water for the jets is provided by a Flow International 20X pump, with dual intensifiers and capable of delivering 385 MPa water at 7.6 liters/min. The waterjets point downward towards the interior cylindrical surface of the drum. The manifold is parallel with and attached to a metal rod which moves a short distance in and out, along the length of the drum. This cyclic movement is driven pneumatically. The waterjet manifold is inclined from the discharge end to the feed end at 10° with respect to the side of the cylindrical drum. This allows the waterjets to be at a decreasing standoff from the drum surface as EM moves down the length of the drum. This arrangement accommodates initially large feed and ensures the waterjets get closer to the drum as the EM cuttings gets smaller and smaller. Positioned at three locations along the length of the cylinder is a circumferential merloned-crenated fence. The height and gap spacing of the three fences decreases from the feed to discharge end. The fences serve to restrict the movement of the solids through the mill, providing an increase in the residence time and therefore cutting effectiveness for the waterjets. The right cylinder portion of the stainless steel drum is 87 cm long and 59 cm OD. A stainless steel cowling at the mill's inlet adds an additional 13 cm to the overall length. The Drum Mill has cut Composition B and PBX-0280, reducing 1-3 kg blocks of the high explosives to kidney bean size chips in minutes. In a continuous flow mode, it is expected the prototype Drum Mill will process about 30 kg/hr.

The high pressure waterjet Drum Mill will quickly and safely reduce the size of diverse EM production wastes providing feed stock suitable for environmentally benign destruction.

In lieu of water, a novel system which uses high pressure liquid nitrogen (LN₂) has been developed at the Idaho National Engineering Laboratory (INEL) to perform cutting and abrading, without the introduction of a secondary waste stream of cutting media. This cryomill is referred to as ZAWCAD, an acronym for Zero Added Waste Cutting, Abrading and Drilling.

The ZAWCAD is similar to abrasive waterjet cutting systems in appearance and function, although the nozzle assembly through which the LN₂ flows is more complex. The working fluid, LN₂, is pressurized to 420 MPa (60,000 psi) and ejected through a small orifice at a flow rate of 0.5-10 liters/min, depending upon the orifice diameter and fluid pressure. The velocity of the stream has been measured at greater than 900 m/s (3,000 ft/s) near the output of the nozzle. In bulk quantities, the LN₂ can be purchased for as little as 6 cents per liter.

The ZAWCAD developers have cut foam-insulation, foodstuffs and ferrous metals and recently, in collaboration with USACERL personnel, have successfully employed the cryomill for the cutting of Composition A5, Composition B, TNT, Benite, M31A1E1 and NOSIH-AA2. A 0.2 mm orifice was employed for the cutting of all EM. The feed rate of energetics into the LN₂ jet was 6 mm/s. Because the LN₂ "cutting fluid" rapidly vaporizes moments after leaving the site of erosive action, the only waste stream from the ZAWCAD is a "dry sawdust" of the material cut. This is, however, a mixed blessing. While no water or other liquid solvent waste stream needs to be subsequently processed for environmentally benign disposal, the dry sawdust (finely powdered EM) from the ZAWCAD does represent a potential explosive hazard, but is definitely manageable.

The ZAWCAD cryomill is a system which clearly warrants continued research and development as a promising technology for both the pretreatment of EM production wastes and the machining (cutting, abrading, milling and drilling) of energetic materials.

REHABILITATION OF TCE-CONTAMINATED UNDERGROUND STORM WATER SYSTEM USING TRENCHLESS TECHNOLOGY

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ABSTRACT

The Naval Air Warfare Center (NAWC) at Trenton, NJ is a gas turbine engine testing facility. Trichloroethene (TCE) is used as a heat exchange medium during engine testing. As part of an on-going environmental investigation program, TCE was found in groundwater and in water discharging from the outfalls of the facility's storm water collection system. Because of high groundwater levels, it was unclear whether the TCE in the outfall discharge was entering the storm sewers via pipe connections and/or from impacted groundwater infiltrating deteriorated sewer lines.

The main storm sewer lines associated with two of the facility's four outfalls, i.e., in the areas of highest TCE concentrations in groundwater, were video inspected. Structural deficiencies ranging from cracked pipe and failed joints to total collapse were found. The rehabilitation of these lines was deemed to be an important part of the facility's remediation plans. Due to the disadvantages associated with conventional pipe excavation and replacement techniques at this site, in-situ rehabilitation alternatives were considered. Cured-in-place pipe (CIPP) technology was selected as the best alternative. This technology involves the formation of a new CIPP inside an existing pipe using a novel "inversion" process.

The disadvantages of excavating contaminated soil to repair the deteriorated storm sewer lines were avoided. Approximately 1,900 lineal feet of pipe, ranging from 8 inches to 27 inches in diameter, were repaired using the CIPP method. A reduction in the infiltration of groundwater into the storm sewer system, and a corresponding reduction in the TCE at the outfall, was observed as a result of the repair work.

1. INTRODUCTION

As part of an on-going remedial investigation (RI) at NAWC Trenton, groundwater and storm water samples were collected in July, 1992. Trichloroethene (TCE) and its degradation products were found in the groundwater and in portions of the storm sewer system. (See Table 1).

Brown & Root Environmental (B&RE) was tasked to investigate the sources and levels of TCE in the storm sewer system and, in subsequent tasks, to inspect and make repairs to portions of the system.

TABLE 1. MAXIMUM CONCENTRATIONS OF TCE DETECTED AT OUTFALLS DURING RI

Outfall No.	TCE Concentration, $\mu\text{g/l}$
001	1,200
002	270
003	14
004	17

$\mu\text{g/l}$ = micrograms per liter (parts per billion)

A field survey and sampling were conducted of all four areas of the site that drain through Outfalls 001 through 004. Inspection of all accessible manholes and inlets identified inconsistencies from the existing sewer drawings and the presence of flow from system connections. Sampling confirmed the presence of TCE in the storm sewer at locations identified during the remedial investigation, predominantly around Bldgs. 40, 41 and 42 that are situated in areas which drain toward Outfalls 001 and 002. In addition, flow of water was observed in the storm sewer during periods of no rain. Infiltration of TCE-containing groundwater to the storm sewers and/or exfiltration of TCE-containing process waters from the storm sewers was indicated. In light of these findings, B&RE's field efforts were focused on the storm sewer lines leading to Outfalls 001 and 002. (See Figure 1).

An illicit-discharge investigation, which included records review, in-field inspection and line tracing, and smoke and dye testing was also conducted to ensure that the storm sewer system was not being compromised by process waters or illicit discharges. Approximately 2,900 lineal feet of pipe in the Outfall 001 and 002 systems were cleaned and inspected. Almost 5 cubic yards of debris were removed. Sections of cracked and collapsed pipe were found. Ninety-five percent of the joints in the uncollapsed piping failed pressure testing and required grouting. Previously unknown connections to the sewer system were found. The illicit-discharge investigation revealed that several process drains and other unidentified lines were connected to the sewer lines. (See Table 2). At this point, B&RE's scope of work was increased to include sewer reconstruction and repair.

TABLE 2. RESULTS OF CLEANING AND INSPECTION - OUTFALLS 001 & 002 NETWORK

- 2,900 Lineal Feet Cleaned and Video Inspected - Obstructions, Offset Joints, Collapsed Pipe Prevented Complete Inspection
- 4.8 Cubic Yards of Debris Removed
- Joints Grouted in 1,512 Lineal Feet of Pipe - 95% of Joints Failed Pressure Test (324 of 342)
- 7 Illicit Connections Found - Rerouted, Plugged or Removed
- 1,900 Lineal Feet Repaired by CIPP Technique

Two subcontractors were procured. One was tasked to perform conventional pipe repair and manhole replacement, and to reroute illicit drain lines and service connections away from the sewer system. Plugging of out-of-service manhole connections and pipe removal were also performed.

A second subcontractor was procured to perform the reconstruction of severely deteriorated sewer lines within the Outfall 001 and 002 systems. To avoid the disadvantages associated with conventional pipe excavation and replacement, in-situ rehabilitation alternatives were considered. A cured-in-place pipe (CIPP) trenchless technology was selected. This rehabilitation proved successful in isolating the sections of the storm water system where it was applied.

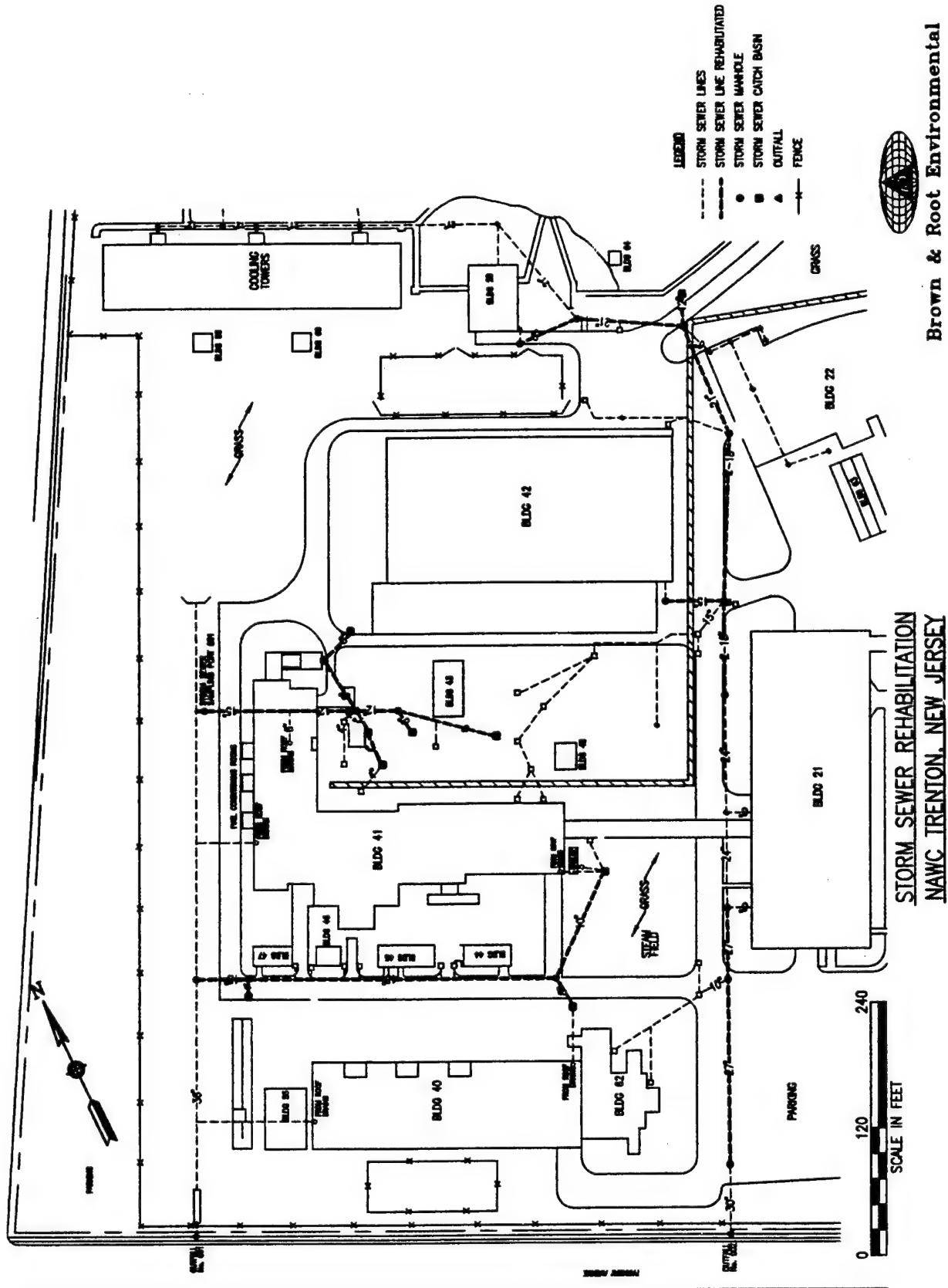


Figure 1. Site Plan of Outfalls 001 and 002 Storm Drainage Area - NAWC Trenton.
Heavy dashed lines indicate sewer lines rehabilitated by CIPP technology.

2. CURED-IN-PLACE-PIPE INSTALLATION

The CIPP technology selected for the NAWC Trenton storm water system rehabilitation was provided by Insituform® of North America. The set up and installation is depicted in Figures 2 an 3. A plastic-coated, needleled felt tube is custom engineered and prefabricated to the desired length and diameter that is required to fit the deteriorated line(s). It is impregnated with a liquid thermosetting resin and shipped to the installation site. A support scaffold with an inversion tube and elbow is set up over a manway leading to the damaged pipe. One end of the prefabricated tube is banded to the lower end of the inversion tube elbow. The inversion tube is then filled with water. The weight of the water inverts the felt tube and forces it to expand inside the damaged pipe. The tube turns inside out and is pressed by the water against the inside walls of the old pipe. The smooth, coated side of the felt tube becomes the new interior surface of the pipe. (Figure 2).

The inversion process results in no relative movement between the felt tube and the old pipe, minimizing damage to the flexible tube material. Also, any incoming or standing water is forced ahead of the inverting tube and out of the pipe. No water that could inhibit proper curing of the resin or alter the shape of the finished pipe is trapped behind the new tube.

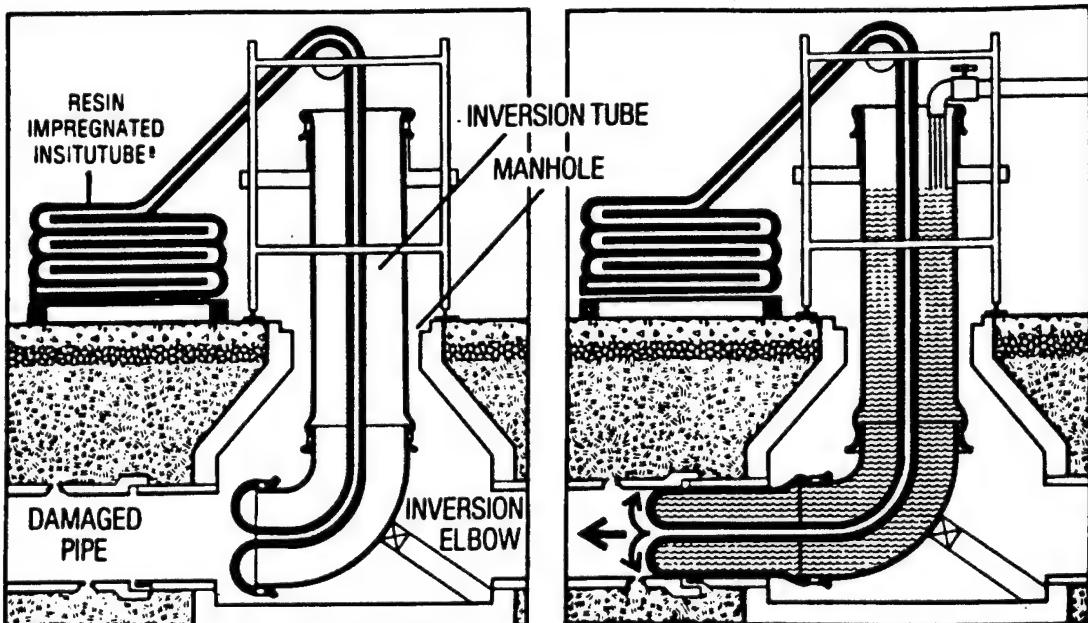


Figure 2. Set Up and Placement of Insituform® CIPP

After the tube is fully inverted through the old pipe, the water used for inversion is circulated (via a hose attached to and drawn into the tube while it is inverting) through a heater to a temperature of approximately 160° F. The hot water causes the thermosetting resin to cure within a few hours. This changes the the pliable felt tube into a hard pipe-within-a-pipe. (Figure 3). The latter has no joints or seams and should be as strong or stronger than the pipe it replaces. The ends of the hardened pipe are cut off and sealed. The inversion tube and scaffolding are removed. Lateral connections to the pipe are restored by a camera-equipped, remotely controlled cutting device.

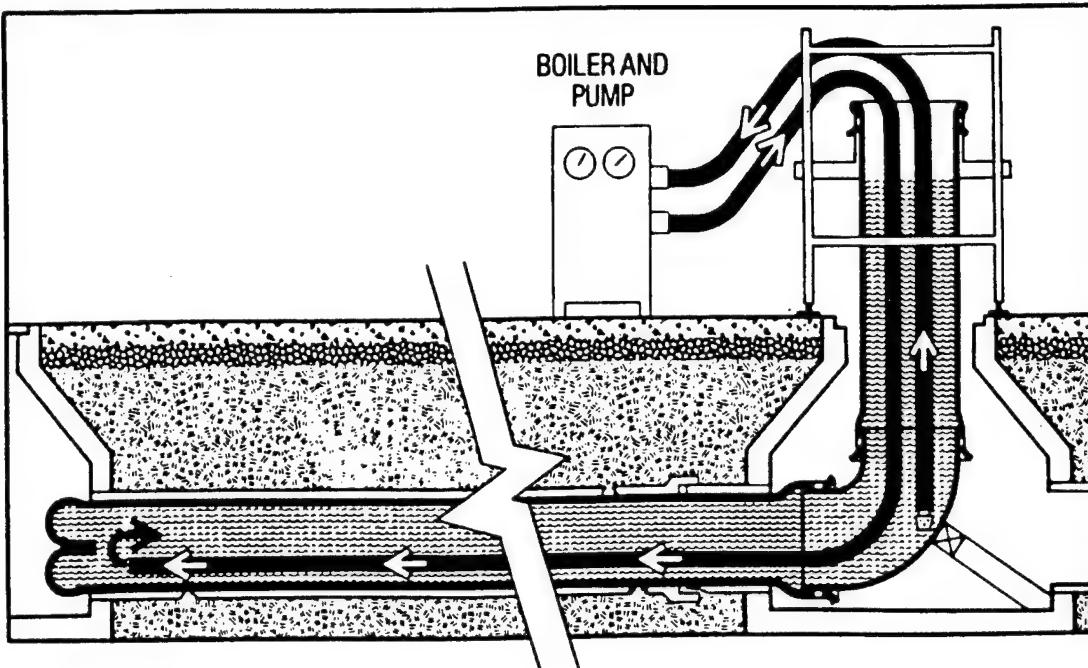


Figure 3. Curing of Insituform® CIPP

Other in situ technologies were considered but were rejected. Hard sleeve liners were not applicable. They would not have eliminated the problem of infiltration of groundwater into the sewer lines, as an annular space would have remained between the liner and the old pipe, nor would they have been able to negotiate the offsets in the deteriorated pipe as had the Insituform CIPP. Expandable PVC pipe, while more flexible than a hard liner, would also not have assured an annular seal nor allowed customization of the resin compound for compatibility with chlorinated solvents, as did the Insituform.

3. ADVANTAGES OF TRENCHLESS TECHNOLOGY

The use of the selected trenchless technology afforded some significant advantages over traditional excavation and repair methods. These are summarized in Table 3.

TABLE 3. ADVANTAGES OF TRENCHLESS TECHNOLOGY
STORM SEWER REPAIR - NAWC TRENTON

- No Pavement or Roadway Excavation
- No Traffic Disruption
- No Excavation, Stockpiling, Sampling and Analyses, Loading, Transport or Disposal of Contaminated Soil
- No Exposure of Construction Workers to Affected Soils or Groundwater
- No Confined Space Considerations
- No Treatment of Groundwater during Installation
- No Joints
- Improved Flow Characteristics

While roadway excavation and traffic disruption were avoided, at this site the advantages gained from a safety and environmental standpoint were even more significant. Costly efforts to maintain environmental and regulatory compliance were unnecessary. Where the trenchless technology was employed, the risks associated with the handling and disposal of contaminated soils and groundwater were avoided. No elaborate environmental safety and health plans were needed. The problems associated with stockpiling, containing, sampling, transporting and disposing of contaminated soils were avoided. Each of these activities involve added cost, and the risk of spills and the exposure of workers and the environment to contaminants. Digging and working in trenches to replace underground piping requires safety measures such as sidewall shoring and, possibly, following confined space entry procedures. The latter were also unnecessary. Further, due to the high groundwater level at this site, it would have been necessary to pump groundwater from the excavations during the pipe replacement. Due to the presence of chlorinated solvents like TCE, the water would have needed treatment prior to discharge, another inconvenience and added expense. Finally, the new pipe eliminates the irregularities in the old pipe's flow path and possesses a lower friction factor, so flow conditions were improved.

4. RESULTS OF SEWER LINE REPAIR

The success of the trenchless technology in repairing and isolating the storm sewer system was observed. While the scope of work did not allow the complete rehabilitation of the 001 outfall system, the 002 outfall system was nearly completely rehabilitated. Measurements of the TCE in the two storm water outfalls from sampling events before and after the pipe repair is shown in Table 4.

TABLE 4. TCE CONCENTRATIONS AT STORM WATER OUTFALLS - NAWC TRENTON

	Before CIPP Repair, $\mu\text{g/l}$ 7/93	After CIPP Repair, $\mu\text{g/l}$ 12/94
Outfall 001	140	130
Outfall 002	90	4(J)

(J) = Concentration below the analytical method detection limit

CONCLUSIONS

Inspection and field tracing studies of the storm sewer lines at NAWC Trenton were carried out. Illicit connections were rerouted or disconnected. Sewer line reconstruction within two of the facility's four outfall systems was done, in part by conventional means and, more significantly, by the application of a CIPP trenchless technology. Those lines repaired using the trenchless technology were successfully isolated from contaminated groundwater as indicated by the reduction in TCE concentration measured at the storm water outfall. Significant advantages from environmental, safety and cost perspectives were realized through the application of the trenchless technology.

ACKNOWLEDGMENTS

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SOIL

FIELD DEMONSTRATION OF A SURFACTANT-ENHANCED SOIL SLURRY BIOREACTOR TECHNOLOGY FOR THE REMEDIATION OF EXPLOSIVES-CONTAMINATED SOIL

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Introduction

Biological treatment of explosives-contaminated soil is currently of interest to the U.S. Department of Defense. Composting is a fully implemented technology capable of removing explosives from soil cost-effectively. The biological and chemical reactions occurring during composting remove 2,4,6-trinitrotoluene (TNT), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), leaving no intermediates. Over the past several years, various groups have examined the use of soil slurry reactors to degrade explosives in soil. Several years of laboratory study have culminated in a pilot demonstration at the Joliet Army Ammunition Plant (JAAP), Joliet, Illinois. Laboratory and field studies (Manning et al., 1995) have demonstrated that TNT, HMX, and RDX can be biologically degraded with molasses as a cosubstrate. Waterways Experiment Station has conducted experiments examining the impact of surfactants on enhancing the degradation of explosives in a slurry reactor. These studies have been encouraging in batch reactor situations. The laboratory studies examined many different surfactants and determined that polysorbate 80 (Tween 80) is the most cost-effective. In addition, Tween 80 can be purchased commercially as a food-grade compound, eliminating regulatory concerns. The laboratory studies also investigated the different concentrations of surfactant in the reactor. The operating conditions were periods of aerobic conditions (with measurable dissolved oxygen), followed by periods of anoxic conditions (with no measurable dissolved oxygen but significant concentrations of nitrate, nitrite, and sulfate). The laboratory studies led to the development of a pilot-scale system to investigate the performance of soil slurry reactors with surfactant enhancement under field conditions. The pilot study at JAAP ran for almost six months. (This was an extension of a previous pilot study conducted at JAAP.) For this work, soil containing TNT, HMX, and RDX in varying concentrations was removed from an area at JAAP designated as Group 61.

System Design

The pilot system is shown in Figure 1. Soil was excavated from Group 61 in areas of TNT contamination. The excavated soil had TNT concentrations of 1,000-7,500 mg/kg, HMX concentrations of 0-300 mg/kg, and RDX concentrations of 0-100 mg/kg. In addition, small amounts of 2,4- and 2,6-dinitrotoluene were in several of the excavated soil samples. The soil was sieved through a 1/4-in. screen to remove rocks, plant roots, and other objects. The material passing through the sieve was used to create a soil slurry (15% or 25% weight/weight in water) that was pumped into 350-gallon stainless steel reactors. The contents were mixed with a 1-hp variable-speed motor with blade-type impellers. Molasses (0.15% on a volume basis; feedlot grade) was added twice weekly in reactors that had molasses added, Tween 80 (3% on a volume basis; food grade) was added once per week in the reactors that had Tween added, and commercial-grade NaOH was added as necessary to maintain pH > 6 but less than 7.

Four reactors were operated. The first was a 25% slurry with a 20% (volume/volume) replacement soil per week, with molasses. The second reactor received 25% slurry with a 20% (volume/volume) replacement soil per week and molasses and 3% Tween 80. The third reactor

was a 15% slurry with a 10% replacement per week; 3% Tween was added to this reactor as the sole cosubstrate and surfactant. The fourth reactor was a 15% slurry with a 10% replacement per week, with molasses and Tween 80. Soil removed from the reactors during replacements was tested for explosives and then subjected to several dewatering schemes. Water removed in dewatering was reused in slurry preparation. This recycled water could be used at least three times before it was discarded after polishing with granular activated carbon.

Analytical Methods

Explosives were analyzed in the soil and water phases by using EPA method 8330. In addition, at the end of the reactor study, small subsamples were removed from the reactors and subjected to a laboratory metabolic study in which the radiolabel carbon-14 was added. Various fractions were identified, including labeled carbon dioxide and other microbial products.

Results

Figure 2 reveals certain trends in the data for the 20% (volume/volume) replacement without surfactants. As indicated in the figure, the adaptation of the microbial system is immediate for TNT. The TNT was removed, and 2-amino-4,6-dinitrotoluene (2A-4,6-DNT) and 4-amino-2,6-dinitrotoluene (4A-2,6-DNT) were generated. As Figure 2 shows, approximately two months were required to achieve TNT concentrations below 20 mg/kg. The 4A-2,6-DNT concentrations were initially around 300-400 mg/kg and decreased to less than 100 mg/kg over the course of the study. The system operated with a high level of consistency, removing TNT to a level of less than 20 mg/kg and also decreasing the concentrations of 2A-4,6-DNT and 4A-2,6-DNT to less than 100 mg/kg.

Figure 3 demonstrates the results from the 20% volume/volume replacement reactor with surfactant as a cosubstrate. Figure 3 demonstrates that the reactor with Tween 80 initially appeared to have slightly improved performance with regard to the degradation of the 4A-2,6-DNT. This reactor did not demonstrate the variation in either TNT removal or 4A-2,6-DNT, as did the molasses-only reactor. During a period of cold weather in early January, the 4A-2,6-DNT concentration increased dramatically, apparently caused by the consortium's inability to process the 4A-2,6-DNT generated by TNT degradation. After the temperature returned to greater than 20°C, the removal of the 4A-2,6-DNT continued. The other two reactors, which operated at a lower soil loading and reduced replacement rate, achieved TNT removal to less than 20 mg/kg. The 4A-2,6-DNT level was less than 50 mg/kg.

The reactor experiments indicated that HMX and RDX concentrations below 10 mg/kg can be achieved. The concentrations of all explosives in reactor liquid (water) fell below 1 mg/L when the temperature was above 25°C and the system was operating to reduce concentrations of soil explosives. It should be noted that during periods of cold weather, TNT removal and levels of 2A-4,6-DNT or 4A-2,6-DNT are impacted.

Small subsamples were obtained from the pilot reactors to determine the metabolism of carbon-14-labeled TNT. The distribution of the radiolabel in the reactor contents was similar in both reactors. Approximately 17-22% of the radiolabel was found in carbon dioxide, indicating mineralization. The remainder was in fatty acids and biomass, which could be removed from the system by increasing the amount of air added to the reactors.

CONCLUSION

The biological soil slurry reactor with molasses and surfactant has the potential to degrade TNT in contaminated soil to levels below 50 mg/kg. HMX and RDX were also removed but at much lower input concentrations. The accumulation of 2A-4,6-DNT and 4A-2,6-DNT was minimized; these compounds were also degraded to levels below 100 mg/kg. In applications of

this technology in cold environments, the temperature of the reactor must be maintained at 20-25°C. Other site-specific issues to be addressed include the residual concentration of explosives allowable in the treated soil and the availability of inexpensive cosubstrates that are effective in promoting microbial activity.

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BIOREMEDIATION FLOW DIAGRAM

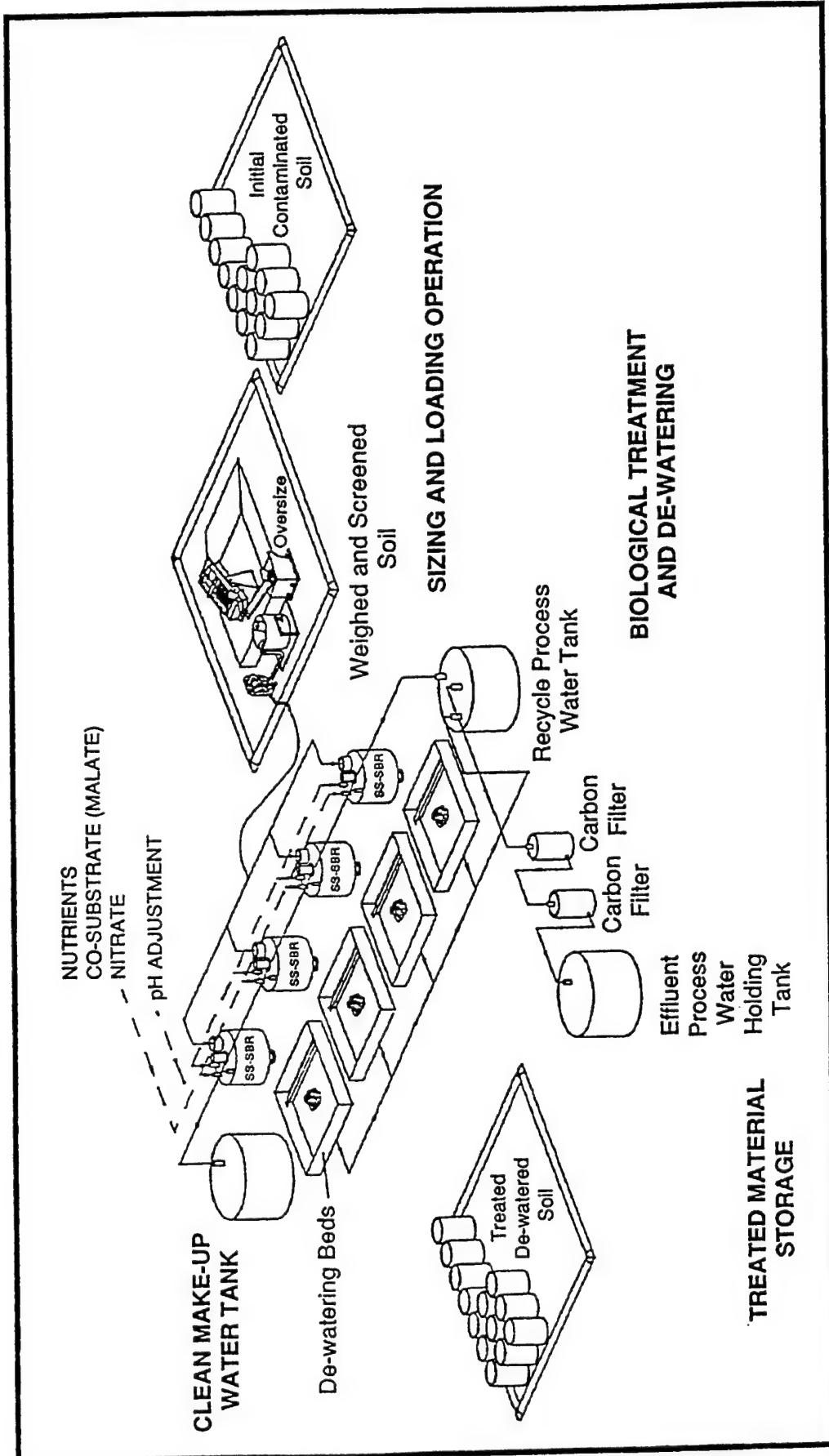


Figure 1 Pilot System

Molasses Bioslurry Reactor

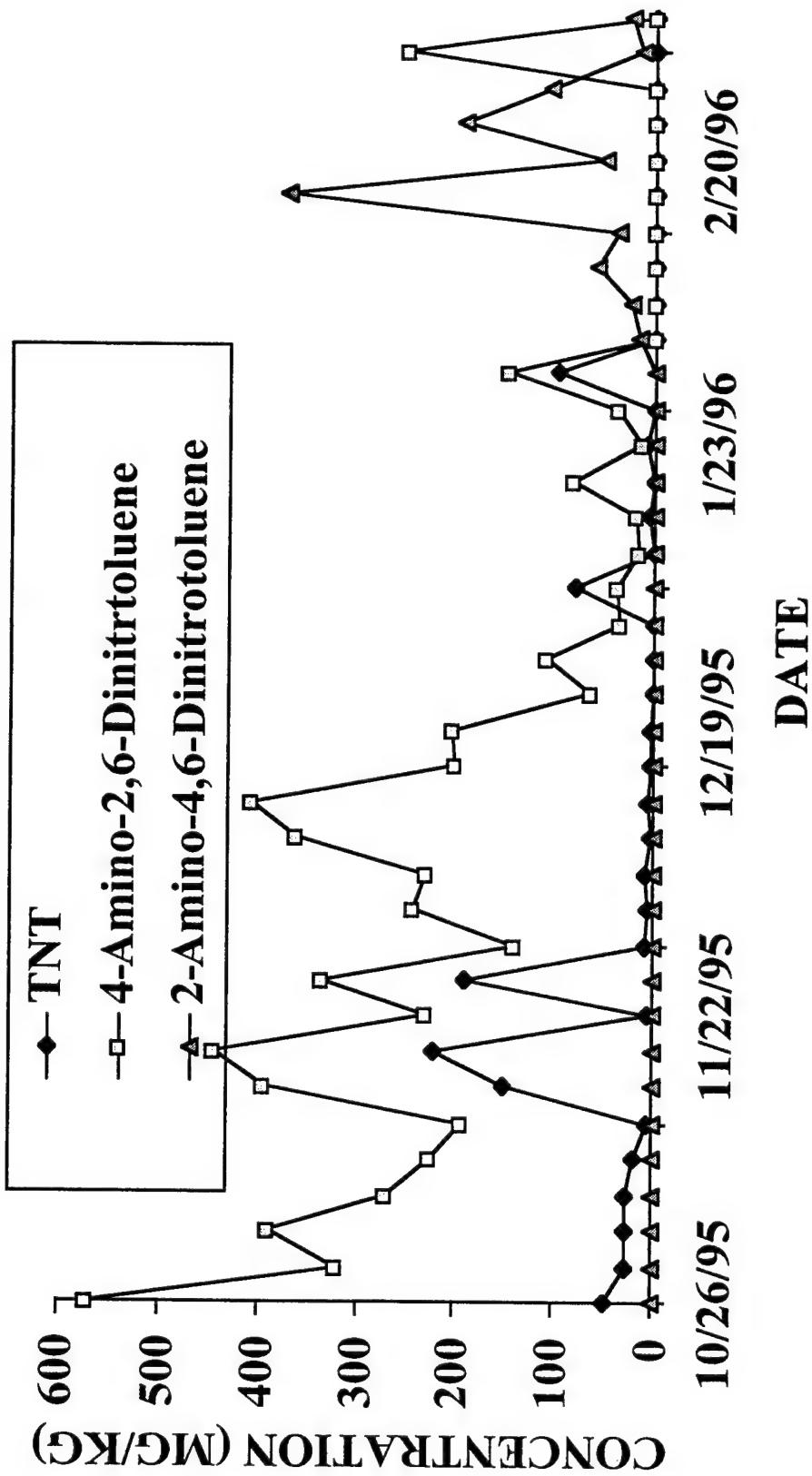


Figure 2 Reactor with 20% Soil Replacement and Molasses

Surfactant Enhanced Degradation

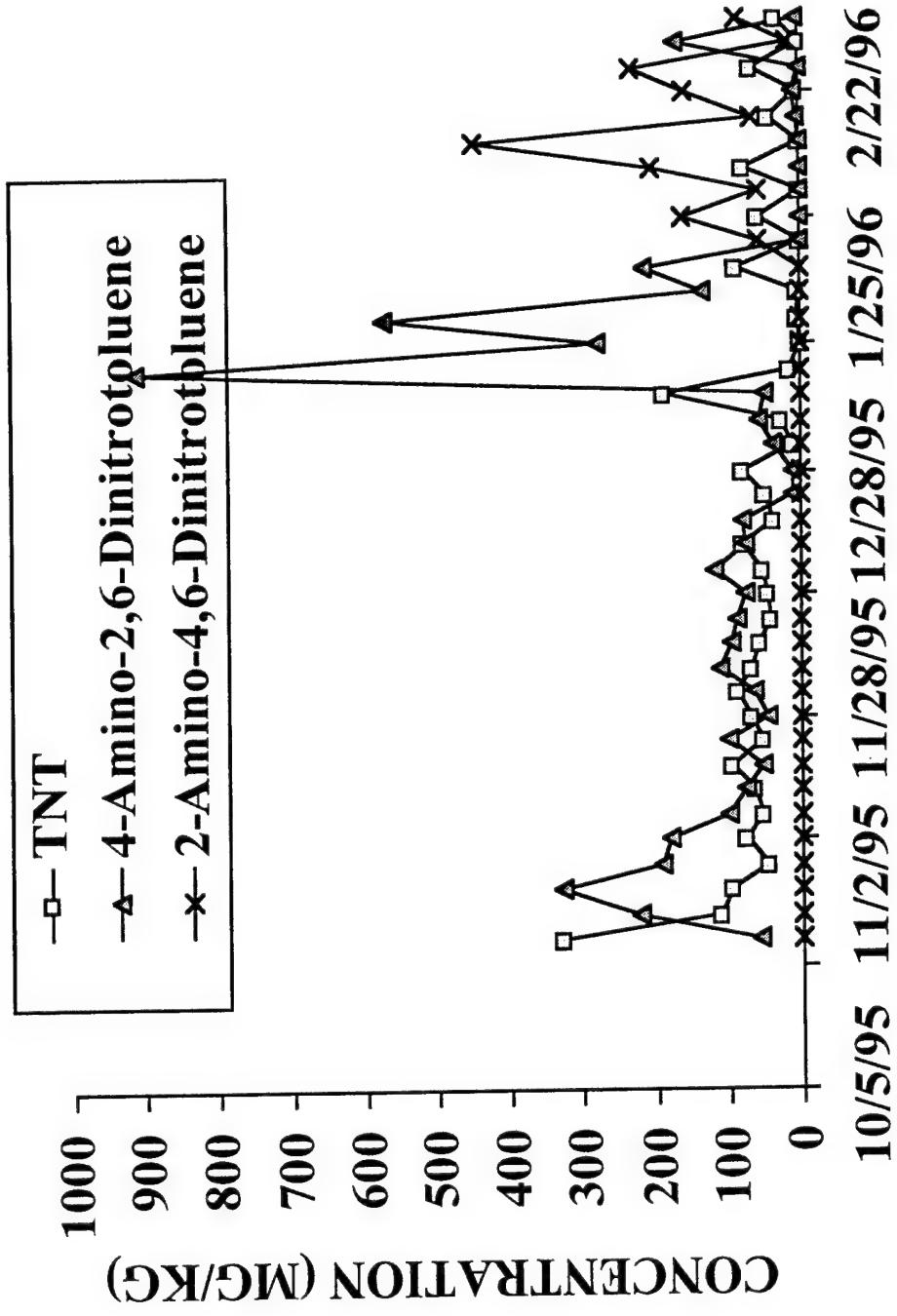


Figure 3 Reactor with 20% Soil Replacement and Surfactant as Cosubstrate

USE OF SHOCK-ABSORBING CONCRETE (SACON) AS AN ENVIRONMENTALLY COMPATIBLE BULLET-TRAPPING MEDIUM ON SMALL-ARMS TRAINING RANGES

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ABSTRACT

Shock-absorbing concrete (SACON) is a low-density, fiber-reinforced, foamed concrete that is used as an energy absorbing material. SACON has found wide applications in the construction of live-fire training villages and the fabrication of target structures. SACON is manufactured by blending sand, portland cement, and water with an aqueous-based foam and a steel or polymer fiber. Typically the resulting concrete will have a density that is approximately one-half that of conventional concrete and an unconfined compressive strength that is one-third to one-fourth that of conventional concrete. SACON offers numerous advantages over wood, rubber tires, or earth berms in trapping bullets on small-arms firing ranges. It will not burn, does not rot, and does not have to be protected from insects. SACON does not erode away, typically maintains an alkaline condition that can slow down metal corrosion and, it is a closed-cell, foamed solid that has low leachability. The current study was undertaken to develop design data for SACON to be used as bullet traps on training ranges. Test blocks were fired on using the M16 rifle with M855 ball ammunition so that the effects of multiple impacts at a single point could be assessed.

The bullet debris that accumulated in thick blocks of SACON did not produce ricochets, even when thousands of rounds were fired at a single point. Pockets or cavities containing bullet debris were developed in some block as shooting continued. The debris deflected incoming bullets upward in the blocks and eventually bullets would crack the top surface of the block. Polypropylene fiber-reinforced SACON performed in a manner comparable to steel fiber-reinforced SACON. Examination of samples of dust produced by the bullet impacts showed that bullet-to-bullet impacts can result in metal particles that can be detected in the dust.

1. INTRODUCTION

The Army is the major service involved in training troops in the use of small-arms (weapons equal to or smaller than 0.50 caliber). Sixty-seven percent of Army firing ranges are small-arms training ranges. The Army currently operates 1,400 outdoor, small-arms ranges in the continental United States and fires over 302 million rounds of small-arms ammunition each year. Military ammunition is fabricated using a full metal jacketed bullet that consists of a brass (copper and zinc) jacket over a hardened lead alloy (lead and antimony) or lead alloy and steel core. Training activities distribute approximately 3139 tons of bullets

into the soil on training ranges annually. Bullets impacting in soil typically fragment and the fragments corrode. The bullet debris and corrosion products become mixed into the soil. The cost of removing metals from soil can range from \$390 to \$650/m³ (\$300 to \$500/yd³). In order to prevent metals from being distributed in the soil it is necessary to trap the bullets and reclaim the metal that would normally be distributed over the training range. Systems for trapping bullets before they enter the soil are being investigated as part of the U. S. Army Environmental Center program for controlling the migration of heavy metals on training ranges and reducing any potential impact on the environment at these training sites¹. The investigation reported here relates to the use of foamed, fiber-reinforced concrete (SACON) as an environmentally compatible, bullet trap.

1.1 SHOCK-ABSORBING CONCRETE (SACON) BULLET TRAPS

SACON traps are made by adding an aqueous foam and fiber to a slurry of sand, portland cement, and water. The light-weight concrete develops a closed, cellular structure that collapses when a bullet impacts the concrete. In a properly designed target system the incoming bullet buries itself in the concrete and does not ricochet². The fiber adds fracture toughness and reduces spalling. The proportions of materials used to prepare SACON with a nominal density of 1,442 kg/m³ (90 lbs/ft³) is given in Table 1. SACON differs from conventional concrete in that no coarse aggregate is used in the mixture and foam and fiber are added to the mixture to reduce the density and reduce cracking and spalling, respectively.

1.2 PHYSICAL PROPERTIES OF SACON

Increasing the amount of fluid-filled void space in concrete lowers its strength. Conventional concrete has a unit weight of approximately 2,560 kg/m³ (160 lbs/ft³), while a typical SACON block (prepared using the proportions given in Table 1) will have a nominal density of 1,440 kg/m³ (90 lbs/ft³). SACON has about one-half the density of concrete. The unconfined compressive strength of conventional concrete is on the order of 21 MPa (3,000 psi); while that of SACON is approximately 6 MPa (870 psi) or one-third the strength of conventional concrete (Table 2). When steel fiber is used as reinforcement the flexural strength of SACON (as measured by the modulus of rupture) is over 3.4 MPa (500 psi)³.

TABLE 1. FORMULATION OF SHOCK-ABSORBING CONCRETE NOMINAL 90 LB/FT³
DENSITY* (1,442 KG/M³)

Cement, Portland Type 1	972 lb/yd ³	577 kg/m ³
Sand (ASTM C 33)	972 lb/yd ³	577 kg/m ³
Water	465.6 lb/yd ³	276 kg/m ³
Aqueous Foam	8.9 ft ³ /yd ³	0.33 m ³ /m ³
Stabilizer	0.27 lb/yd ³	0.16 kg/m ³
Steel Fiber	193 lb/yd ³	115 kg/m ³

* Actual density after addition of steel fiber is 97 lb/ft³ (1,554 kg/m³)

1.3 CHEMICAL PROPERTIES OF SACON

SACON is designed using Type I portland cement and can be expected to have the chemical characteristics associated with conventional concrete made with this same cement. In the hardening process in concrete the calcium silicate phases in the cement react with water to form calcium silicate hydrate gel and calcium hydroxide. The predominant calcium silicate phase present in Type I portland cement is tricalcium silicate (typically 50 percent of the cement by mass). During hydration the tricalcium silicate will produce 21 kg of calcium hydroxide for every 100 kg of tricalcium silicate (or 21 kg of calcium hydroxide for every

TABLE 2. PHYSICAL PROPERTIES OF 90 LB/FT³ DENSITY* STEEL FIBER REINFORCED SHOCK-ABSORBING CONCRETE

Unconfined Compressive Strength	psi	MPa
7 day age	663	4.57
28 day age	836	5.76
60 day age	956	6.59
<u>Flexural Strength</u>		
28 day age	565	3.90
60 day age	525	3.62

* 90 lb/ft³ is the nominal density, actual density is 97 lb/ft³

200 kg of cement reacted). Hardened concrete will generally react very slowly with the carbon dioxide in the air and over the course of years the solid mass will drop in alkalinity with the center of the concrete mass being affected last⁴. Concrete made with portland cement can be expected to remain alkaline for years under normal atmospheric exposure. While the low density of SACON could increase the rate of gas diffusion, the high cement content in SACON will work toward maintaining alkalinity.

1.4 BULLET-TRAPPING PROPERTIES OF SACON

SACON has a cellular structure and projectiles impacting on SACON crush the cells as they enter the solid. The effects of fractures propagating from the impact point are minimized by the fibers cast into the foamed concrete matrix. The depth of penetration of a bullet into SACON depends on the shape, cross-section, density, pattern of deformation, and the kinetic energy of the bullet. The complicated nature of the interaction of these factors has caused most investigators to rely on empirical data obtained in live-fire testing as a basis for designing bullet-stopping structures. The most common data obtained in a live-fire test is the apparent depth of penetration, the distance from the surface of the SACON to the rear of the embedded bullet. Table 3 shows typical penetration depths observed when a variety of rounds are fired at close range (less than 6 m) into 1,442 kg/m³ (90 lb/ft³) SACON.

TABLE 3. DEPTH OF BULLET PENETRATION IN 90 LB/FT³ *
STEEL FIBER-REINFORCED SACON

Weapon	Average Penetration	
	inches	mm
0.38-cal pistol	1	25
0.45-cal pistol	1.25	32
9-mm pistol	2.37	60
M-16 A2 rifle (5.56 mm 56 grain ball)	2.5	64
M-16 A2 rifle (5.56 mm 62 grain penetrator)	2.8	71

* Nominal Density - Actual Density is 97 lb/ft³ (1,554 kg/m³)

In designing SACON bullet-traps, the depth of penetration of a particular round is only one consideration. The objective of a trap is to successfully contain the fired bullet. The SACON must be of such low density that the bullet will not ricochet even when striking the surface at a low angle. Intact bullets are less of a problem for containment than bullet fragments. Traps that do not cause the bullets to shatter or separate the core and jacket are preferred. These additional considerations make live-fire testing a necessary starting point for any bullet trap design effort.

2. LIVE-FIRE TESTING PROGRAM

Most small-arms training in the Army is conducted with the M16A2 rifle firing the M855, 5.56-mm ball cartridge. The M855 round has a fully brass-jacketed, 4-g (62-grain) pointed-tipped bullet. The bullet contains a steel cone and a lead slug. Live-fire tests were undertaken using this cartridge with the following objectives:

- Establish the depth of penetration for single and multiple impacts at a single point on the bullet-trapping block.
- Determine if bullet-debris accumulating in the SACON bullet trap will result in the production of ricochets that could be a hazard to the shooter.
- Determine the effect of fiber type on the depth of penetration.
- Make a preliminary assessment of the composition of dust generated in bullet-to-SACON and bullet-to-bullet impacts.

2.1 TEST SPECIMENS AND TEST METHODS

Concrete samples were prepared by mixing the components in the proportions indicated in Table 1. One specimen prepared with the identical formulation and polypropylene fiber added at a rate of 7 kg/m³ (12 lbs/yd³) was available from an earlier test sequence. All specimens were cured in a 100 percent humidity condition at 23 °C for 28 days.

All live-fire testing was done at an outdoor range, with the shooter-to-target distance maintained at 6 m (18 ft). The rifle used was bench-mounted and equipped with a telescopic sighting device that allowed the

bullets to be grouped within a 5-cm (2-in.) circle. All rounds were fired perpendicularly into the target block. The test blocks were placed in a plexiglass enclosure with a bullet port in front of the impact point. The dust that was produced by the bullet impacts collected in front of the target block and could be periodically sampled. At selected intervals during the shooting, the apparent depth of penetration of the bullet hole was determined by measuring the lateral distance a 4-mm diameter wooden rod could be pushed into the bullet hole before it encountered resistance.

After the live-fire testing was completed selected test blocks were injected with urethane foam to hold the bullet debris in place and cut into halves vertically along the bullet path using a diamond saw. The blocks were photographed and the size of the cavity was determined by removing portions of the bullet debris contained in the block.

Selected dust samples were pressed into pellets and coated with carbon, and analyzed using an Electroscan 2020 scanning electron microscope equipped with a Princeton Gamma Tech Prism, digital x-ray spectrometer. The surfaces of selected pellets were mapped using a Princeton Gamma Tech microanalysis unit attached to a Hitachi S2500 scanning electron microscope to determine the distribution, composition, particle size, and shape of metal fragments present in the dust.

2.2 RESULTS

Table 4 summarizes the data obtained on penetration from successive bullets fired at the same point. All blocks less than 46 cm (22 in.) thick were shot through front-to-back with fractures occurring at the rear of the blocks. In blocks that were 56-cm thick or thicker, the bullet debris accumulated at a depth ranging from 25 to 48 cm (10 to 19 in.) and subsequent bullets were deflected upward inside the block. When blocks thicker than 56 cm (22 in.) showed failure, the fractures occurred at the top of the block, not on the rear surface.

TABLE 4. RESULTS OF LIVE FIRE TESTING

Specimen Designation	Thickness cm (in.)	Maximum Depth of Penetration cm (in.)	Number of Rounds Fired	Remarks
12B	30.5 (12)	30.5 (12)	12	Back of block failed.
12C	30.5 (12)	30.5 (12)	21	Back of block failed
12D	30.5 (12)	22.8 (9)	30	Block removed for examination
12E	30.5 (12)	29.2 (11.5)	81	Back of block failed
24A	57.2 (22.5)	25.4 (10)	370	Top of block failed
24B	57.2 (22.5)	47.8 (18.8)	570	Top of block failed
36	91.4 (36)	46.2 (18.2)	1,800	Top of block failed
22 Poly*	57.2 (22.5)	45.7 (18)	5,800	Block removed for examination

* Polypropylene fiber used in this block

No ricochets occurred at any point in the live-fire testing program. A SACON block that was prepared with polypropylene fiber was hit at one impact area with 5,800 bullets and although an extensive cavity containing bullet debris developed (Figures 1 and 2), no ricochets were produced. The mass of compacted bullet debris was evident when the block was cut apart, but the mass had been impacted by incoming rounds thousands of times during the test without forcefully deflecting a bullet out of the block.

The single polypropylene fiber-reinforced SACON block that was tested behaved in a manner similar to the steel fiber-reinforced SACON. The depths of penetration were comparable and the deflecting effect of the bullet debris was similar to the effect observed in the blocks containing steel fiber.

The preliminary analysis of the dust ejected from a block that had been hit at four separate impact points (only bullet-to-SACON impacts) showed that the dust is primarily sand and hydrated cement (Figure 3). Dust from a block that had taken 30 bullet impacts at a single point (producing a significant number of bullet-to-bullet impacts) showed detectable fragments of lead and copper (Figure 4).

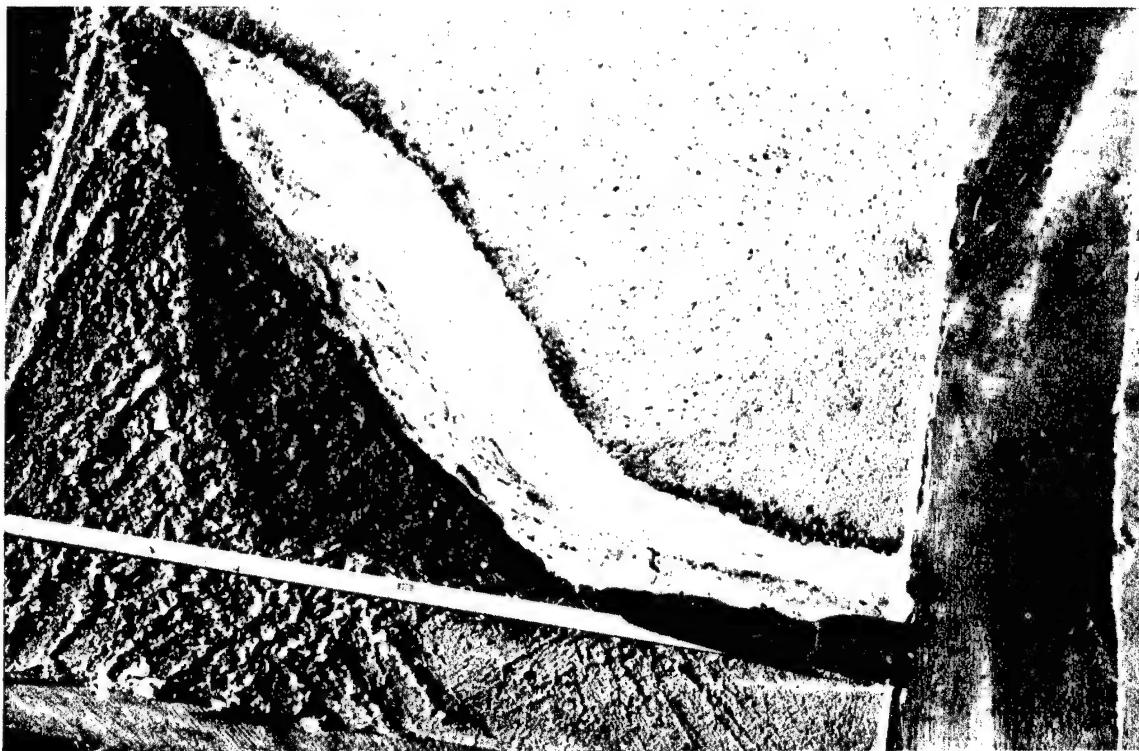


Figure 1. SACON block impacted by 5,800 bullets. The cavity was filled with white urethane foam prior to cutting the test block. The point of entry is the lower right end of the foam mass. The dark grey material to the left is bullet debris.



Figure 2. Close-up of cavity in SACON block. The cavity extended over 10 cm from the center line of the bullet path. The point of the trowel is resting on a mass of bullet debris.

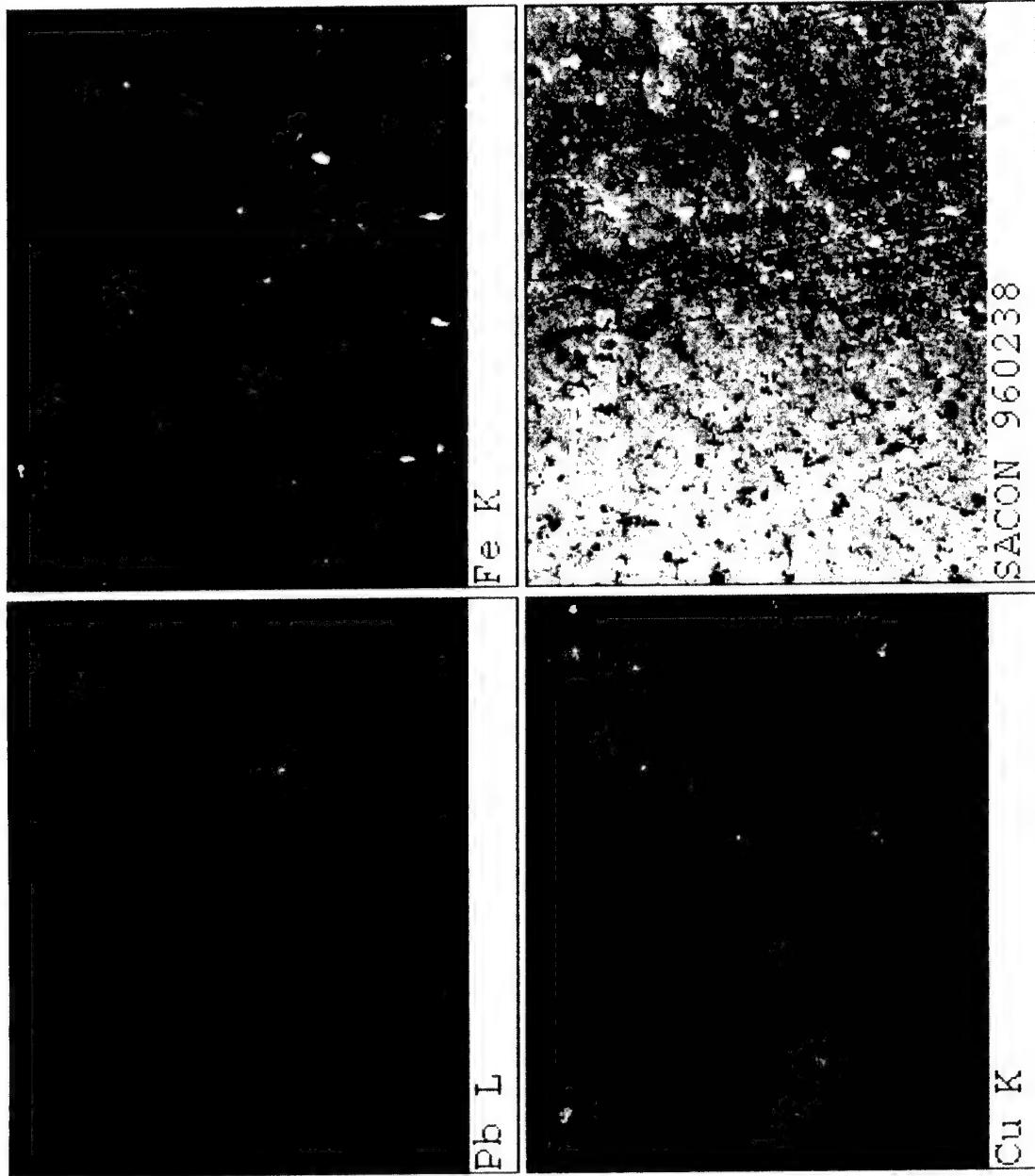


Figure 3. Electron-excited x-ray fluorescence maps showing metal distribution in the dust from a block having only bullet-to-SACON impacts. Very few particles are imaged by the characteristic radiation from lead or copper. The image on the lower right is the electron-backscatter image of the surface of the powder pellet. Bulk analysis using x-ray fluorescence showed no measurable lead (estimated at less than 0.1% by mass) and 0.3% by mass copper.

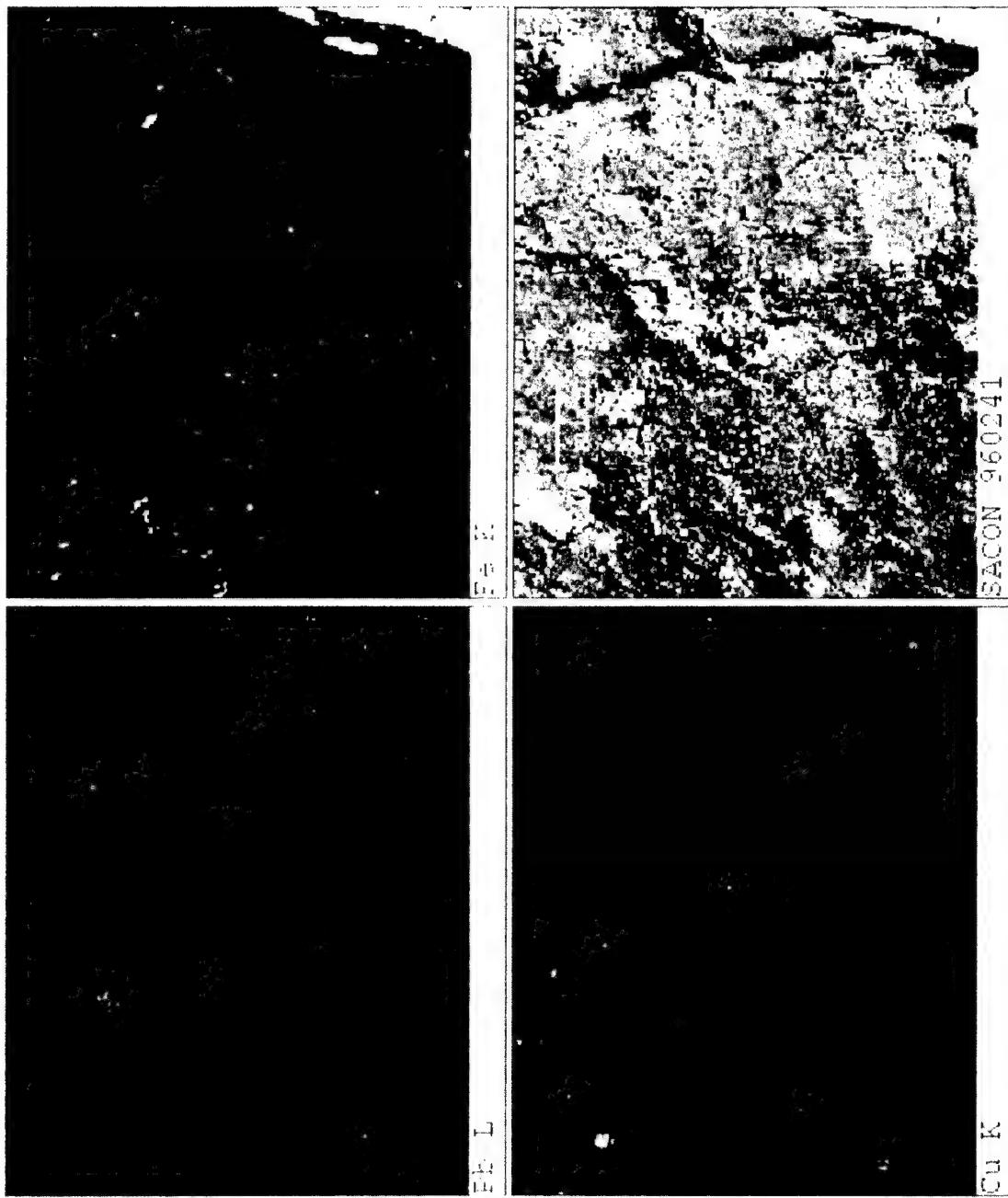


Figure 4. Electron-excited x-ray fluorescence maps showing metal distribution in the dust from a block from a single point with 30 bullets. Block was hit at a single point with 30 bullets. A large number of particles are imaged by the characteristic radiation from lead or copper. The image on the lower right is the electron-backscatter image of the surface of the powder pellet. Bulk analysis using x-ray fluorescence showed 3.2% by mass lead and 1.1% by mass copper.

CONCLUSIONS

The investigations of SACON reported here indicate that multiple bullet impacts at a single point can produce a dense mass of bullet debris inside a thick SACON bullet-trapping block. The debris does not produce ricochets; and can deflect the subsequent bullets upward inside the block. The bullet deflection can cause blocks to eventually fail at the top surface rather than the rear surface. The polypropylene fiber-reinforced SACON showed penetration and bullet-trapping characteristics that were basically similar to those observed with steel fiber-reinforced SACON. The preliminary examination of dust from bullet-to-SACON impacts showed negligible metal debris. Dust from blocks where a significant number of bullet-to-bullet impacts occurred contained detectable fragments of copper and lead.

ACKNOWLEDGMENTS

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ISOLATION AND CHARACTERIZATION OF BACTERIA THAT DEGRADE NITROGLYCERIN

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ABSTRACT

Six strains of bacteria capable of degrading nitroglycerin (NG) were isolated from soil previously exposed to NG. Nitroglycerin degradation by each of the strains was characterized, with representative degradation patterns reported for two strains, *Pseudomonas putida* I-B and *P. putida* II-C. It was found that *P. putida* I-B denitrated NG into isomers of MNG with a preference for the denitration of nitroglycerin at the C2 position. *P. putida* II-C denitrated NG in a random fashion, producing a mixture of DNG isomers and a mixture of MNG isomers. Both strains liberated nitrite as a product of NG denitration. All six isolates were tested for their abilities to tolerate up to 3.96 mM NG. Nitroglycerin concentrations up to 1.32 mM did not inhibit growth of the six NG-degrading isolates, whereas the growth of *P. syringae* pathovar *syringae*, an organism not previously exposed to NG, was inhibited at 0.44 mM NG. The growth of one NG-degrading isolate was uninhibited at 3.52 mM NG and only partially inhibited at 3.96 mM NG.

INTRODUCTION

Nitroglycerin (NG), or glycerol trinitrate, is one of the most widely used explosives. It is the main component of dynamite and it serves as a plasticizer for nitrocellulose in smokeless, doublebase propellants (1, 2). Medicinally, nitroglycerin is a vasodilator, and has been used for the treatment of angina pectoris (1).

The discharge of process water from nitroglycerin manufacture poses an environmental threat, especially to aquatic ecosystems. It has been estimated that a full production nitroglycerin manufacturing plant releases 35.3 mg of NG per liter of waste water, discharging over 166,000 liters of waste water daily (2). With a solubility of 1.8 g l⁻¹ in water at 20 °C (1), nitroglycerin is easily transported throughout the environment. Biological impact studies of ponds that received munitions-manufacturing waste water at the Badger Army Ammunition Plant (BAAP), in Baraboo, WI, revealed that nitroglycerin manufacturing wastes exerted toxic effects on algal and macroinvertebrate populations. The algal species identified at NG-contaminated study sites were characterized as pollution tolerant, and populations of benthic macroinvertebrates were absent, both indicating toxic environmental conditions (3).

Whereas nitroglycerin exerts toxic effects on organisms ranging from bacteria to mammals, various studies have demonstrated that NG is amenable to biological breakdown (2). Because NG has been administered to humans for medicinal purposes, its physiological effects were originally studied in mammals. By orally administering ¹⁴C-labeled nitroglycerin to rats, it was determined that NG was metabolized via two pathways. The first pathway consisted of the stepwise denitration of NG to dinitroglycerin (DNG), mononitroglycerin (MNG), and glycerol, which was ultimately oxidized to CO₂. Through a second pathway, denitration products were conjugated to glucuronic acid (4). In an *in vitro* study, in which rat liver homogenates were incubated with ¹⁴C-labeled nitroglycerin, the enzyme glutathione-organic nitrate reductase was implicated in the stepwise denitration of NG (5). Partially purified preparations of this rat liver enzyme denitrated nitroglycerin in the presence of reduced glutathione. One molecule of NG reacted with two

glutathione molecules to release an inorganic nitrite ion from either the C2 or the C3 position of nitroglycerin, forming 1,3-DNG or 1,2-DNG, respectively (6). In another *in vitro* study, it was found that the plasma membrane fraction of bovine coronary smooth muscle cells enzymatically denitrated NG, with a concurrent release of nitric oxide (7).

More recently, work has been conducted to characterize the NG-degradation ability of the white-rot basidiomycete, *Phanerochaete chrysosporium*. Servant *et al.* (8) demonstrated *in vivo* that NG was aerobically degraded into DNG and MNG, with the liberation of nitrite ions and nitric oxide. Upon release, a fraction of the nitrite was rapidly oxidized to nitrate, while the remaining nitrite was reduced to nitric oxide and detected as complexes with non-heme iron-sulfur centers. These nitric oxide complexes were the same as those normally formed during nitrite metabolism by *P. chrysosporium*. Nitric oxide was also detected as a complex with a reduced heme, possibly as a direct NG-denitrification product released through an as yet uncharacterized pathway. Because nitrate ions were not directly released through NG denitrification, the authors hypothesized that denitrification occurred via a reduction reaction catalyzed by a glutathione S-transferase-type system, similar to that previously characterized in mammalian systems, rather than by an esterase reaction.

To further characterize fungal nitroglycerin metabolism, *in vitro* NG degradation by crude cell extracts and by subcellular fractions of *P. chrysosporium* was studied (9). Based on these studies, 30 percent of the cytosolic NG-denitrification activity was attributed to a glutathione S-transferase system. Additional anaerobic, NADPH-dependent, reductive nitroglycerin denitrification, found in cytosolic and microsomal subcellular fractions, was believed to be a result of cytochrome-P450 activity. Microsomal subcellular fractions were also noted to contain anaerobic, Fe^{2+} -dependent NG-denitrification activity, surmised to be related to an additional hemoprotein enzyme system. This Fe^{2+} -dependent NG degradation system released nitric oxide as an NG-denitrification product. Thus, multiple enzymatic systems are involved in the denitrification of nitroglycerin by *P. chrysosporium*. Further, the observation that the fungus *Geotrichum candidum* cleaved nitrite groups from the NG molecule with a regioselectivity different from that of *P. chrysosporium* (10, 11) suggests that other, yet uncharacterized NG-degradation pathways may exist among additional species of fungi.

Several studies have been conducted to investigate the ability of bacteria to degrade nitroglycerin. In an initial study, Wendt *et al.* (12) found that both mixed and pure bacterial cultures, obtained from domestic sewage activated sludge, were capable of degrading NG in a stepwise fashion, via the di- and monoesters. Cultures were unable to utilize NG as a sole carbon source, and no attempts were made to identify the organisms involved or to characterize enzymatic pathways. A follow-up study (13), in which a mixed bacterial culture was assayed for its ability to degrade nitroglycerin, confirmed the findings of Wendt *et al.* (12), that bacteria were unable to utilize NG as a sole carbon source. More recently, NG-degrading strains of *Bacillus thuringiensis/cereus*, *Enterobacter agglomerans* (14), and *Agrobacterium radiobacter* (15) have been identified.

A primary goal of our laboratory is to provide a detailed characterization of bacterial enzyme systems used to degrade nitroglycerin. Toward this goal, we discuss the *in vivo* characterization of six strains of NG-degrading bacteria. Attention is focused on two isolates, one which denitrates NG preferentially into 1,3-DNG and 1-MNG, and another which randomly denitrates NG into a mixture of DNG and MNG isomers. In addition, the culture densities attained by these isolates in medium containing 0-3.96 mM nitroglycerin are compared.

METHODS

Materials: Nitroglycerin, dissolved in water at concentrations of 4.40 mM and 6.60 mM, was obtained from Olin Corporation. Analytical reference standards of NG, 1,2-DNG, 1,3-DNG, 1-MNG, and 2-MNG were purchased from Radian. Spizizen minimal (SM) phosphate salt medium (16), adjusted to pH 7.0, was used for the cultivation of all strains. As noted, various concentrations of nitroglycerin were added to SM medium, and $(NH_4)_2SO_4$ was omitted from the medium as indicated. All incubations were conducted aerobically, at 30 °C. Aerobic liquid

cultures were shaken at 250 RPM in a New Brunswick water bath shaker. Optical densities of cultures were determined with a Klett-Summerson photoelectric colorimeter, using a red filter.

Isolation of nitroglycerin-degrading bacteria: Soil samples were collected at BAAP from sites previously contaminated through nitroglycerin manufacturing processes. Bacteria capable of degrading nitroglycerin were isolated based on two characteristics: their ability to utilize NG as a sole source of nitrogen and their ability to tolerate NG concentrations inhibitory to the growth of most bacteria.

For the isolation of bacteria capable of utilizing NG as a nitrogen source, soil samples were used to inoculate liquid SM medium lacking $(\text{NH}_4)_2\text{SO}_4$ but supplemented with 0.44 mM NG. An enrichment technique was used to isolate bacteria capable of tolerating NG concentrations inhibitory to other organisms. SM-medium starter cultures, inoculated with soil, were used to successively inoculate a series of SM cultures containing the following increasing amounts of nitroglycerin: 0.13 mM, 0.22 mM, 0.44 mM, 0.88 mM, 1.10 mM, 1.32 mM, and 2.20 mM. The isolated organisms were then assayed for their abilities to degrade NG.

Identification of nitroglycerin-degrading bacteria: NG-degrading bacteria isolated at BAAP were identified based on morphological observations, the API 20E identification system for gram negative bacteria (bioMerieux), as well as additional physiological tests.

Cultivation conditions used to evaluate NG degradation by the BAAP isolates: Starter cultures (SM medium supplemented with 1.32 mM nitroglycerin) were used to inoculate triplicate SM-medium cultures, supplemented with 1.32 mM NG, to 10 Klett Units (K.U.). At recorded intervals, the optical density of each culture was measured, and a sample was removed for NG-denitrification analysis. Cells were removed from samples by centrifugation and the supernatant fluid was stored at -80 °C until analyzed by high-performance liquid chromatography (HPLC).

Nitroglycerin toxicity: Each BAAP strain (SM-medium starter culture grown without NG) was inoculated to 10 K.U. into a duplicate series of flasks containing SM medium supplemented with one of the following nitroglycerin concentrations: 0 mM, 0.44 mM, 0.88 mM, 1.32 mM, 1.76 mM, 2.20 mM, 2.64 mM, 3.08 mM, 3.52 mM, and 3.96 mM. The cultures were incubated for 24 hours, at which point, turbidity was measured.

Analytical methods: Samples were analyzed for the presence of NG, 1,3-DNG, 1,2-DNG, 2-MNG, and 1-MNG by HPLC (Beckman). The UV detector was set at 204 nm. Samples were injected onto a 4 μm Nova-Pak radial compression C₁₈ column (length, 100 mm; diameter, 5 mm [Waters]) and eluted with a methanol-water step gradient, at a flow rate of 1.25 ml/min (17, 18). Isomers of MNG were resolved in a mobile phase consisting of five percent methanol, isomers of DNG were resolved in 30 percent methanol, and NG was eluted in 65 percent methanol. The analytical column was protected by a 0.5 μm precolumn filter (Upchurch Scientific) and a 5 μm ODS Safeguard guard cartridge (MetaChem Technologies).

Samples were analyzed for the presence of nitrate and nitrite by ion chromatography. A Dionex DX-100 Ion Chromatograph with conductivity detector was used. Samples were injected onto an AS4A Dionex IonPac column (length, 250 mm; diameter, 4 mm), protected by a Dionex AG4A guard column (4 mm). The mobile phase consisted of 1.8 mM sodium carbonate and 1.7 mM sodium bicarbonate, run at a flow rate of 2 ml/min.

RESULTS

Strain isolation and identification: Six different strains of NG-degrading bacteria, based on colony morphology, were isolated and chosen for additional study. These strains were designated

I-A, II-A, I-B, II-B, I-C, and II-C. Two strains (I-B and I-C) were isolated based on their abilities to utilize NG as a nitrogen source, while the other four strains were isolated through enrichment procedures. All six strains were gram negative rods. Strain I-A was identified as *Klebsiella oxytoca*, strains II-A and I-C were identified as *Pseudomonas fluorescens*, and strains I-B, II-B, and II-C were identified as *P. putida*.

NG degradation by the BAAP isolates: Time course experiments were used to characterize pathways by which the six BAAP isolates degraded nitroglycerin. By omitting glucose from SM medium containing nitroglycerin, it was determined that none of the isolates would grow when provided with NG as the sole carbon source. In the absence of $(\text{NH}_4)_2\text{SO}_4$, all isolates were able to utilize nitroglycerin as a nitrogen source, however growth rates and final cell yields increased with the inclusion of $(\text{NH}_4)_2\text{SO}_4$ (data not shown). Further, cultures of *P. putida* strains I-B and II-C lacking $(\text{NH}_4)_2\text{SO}_4$ took twice as long to denitrify 1.32 mM nitroglycerin as cultures provided with $(\text{NH}_4)_2\text{SO}_4$ (data not shown). Fig. 1 shows the denitrification of 1.32 mM nitroglycerin and its intermediates, over 24 hours, by *P. putida* strains I-B and II-C. Of note is the observation that NG-denitrification enzymes used by these two strains removed nitrite groups from nitroglycerin with differing regioselectivities. *P. putida* I-B regioselectively denitrated nitroglycerin into 1,3-DNG and 1-MNG (Fig. 1a), while *P. putida* II-C (Fig. 1b) denitrated NG into a mixture of 1,3- and 1,2-DNG and a mixture of 2- and 1-MNG. More specifically, *P. putida* I-B denitrated NG into 1,3-DNG/1,2-DNG with a ratio of 7.6, whereas *P. putida* II-C denitrated NG into 1,3-DNG/1,2-DNG with a ratio of 0.5. *K. oxytoca* I-A and *P. fluorescens* strains II-A and I-C denitrated NG regioselectively, favoring removal of nitrite from the C2 position of nitroglycerin, while *P. putida* II-B denitrated NG in a non-regioselective fashion (data not shown).

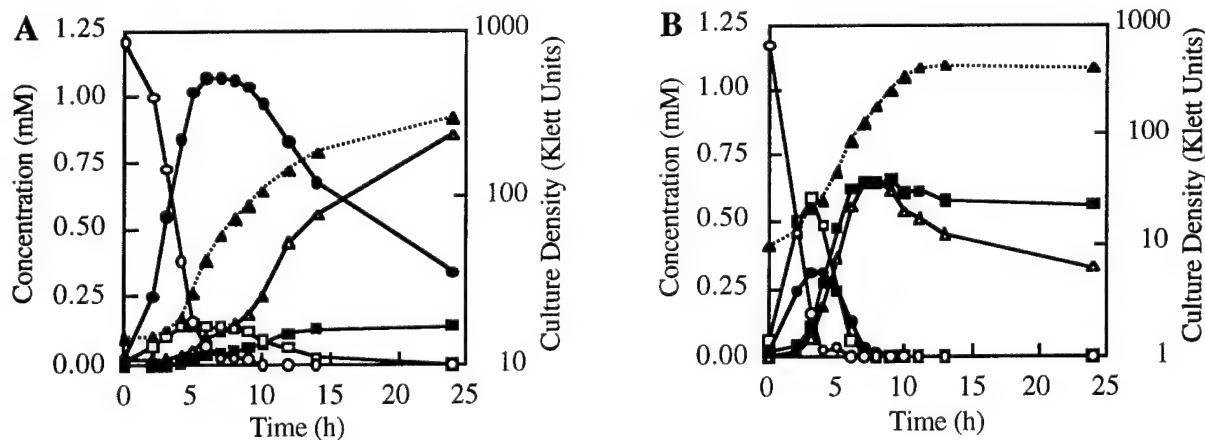


Figure 1. Time course of NG degradation and culture growth by (a) *P. putida* I-B and by (b) *P. putida* II-C. NG was provided at an initial concentration of 1.32 mM. Values are the averages of three independent experiments. \circ , NG; \bullet , 1,3-DNG; \square , 1,2-DNG; \blacksquare , 2-MNG; \triangle , 1-MNG; \blacktriangle , culture density.

Analyses were conducted to determine whether *P. putida* strains I-B and II-C liberated nitrate or nitrite as a product of nitroglycerin denitrification. These experiments demonstrated that both strains liberated nitrite (Fig. 2). For both strains, the concentrations of nitrite that accumulated were approximately stoichiometric to the amounts of NG degraded and to the amounts of NG-degradation intermediates remaining in the medium. Significant amounts of nitrate were not

detected in the growth medium of either strain. Through control experiments, in which *P. putida* strains I-B and II-C were grown in SM medium supplemented with 2.64 mM NaNO₃ or NaNO₂, it was confirmed that neither strain reduced nitrate to nitrite or oxidized nitrite to nitrate, under the routinely employed culture conditions.

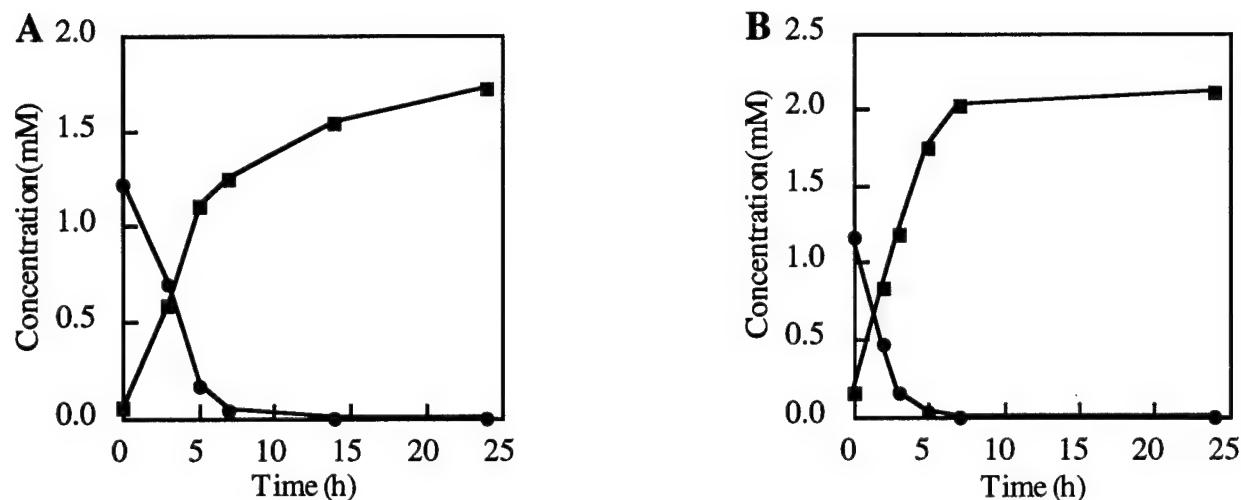


Figure 2. Time course of NG degradation and nitrite accumulation by cultures of (a) *P. putida* I-B and by cultures of (b) *P. putida* II-C. Values are the averages of three independent experiments. ●, NG; ■, nitrite.

To verify that NG-breakdown was enzymatic, rather than a result of spontaneous degradation, cell-free control reactions were incubated under normal culture conditions without a notable decrease in nitroglycerin concentration. Heat-killed cells, incubated for 24 hours in SM medium supplemented with 0.88 mM NG, caused no significant decrease in culture-medium nitroglycerin concentrations. This demonstrated that NG did not adhere to the surface of non-viable cells. In addition, nitroglycerin was not degraded by medium from NG-degrading cultures after passage through a 0.45 μ m filter, implying that extracellular enzymes are not involved in this process.

Nitroglycerin toxicity: For this work, we defined nitroglycerin toxicity as the inhibition of bacterial growth as measured by culture turbidity. The nitroglycerin-degrading bacteria isolated at BAAP exhibited varying degrees of tolerance to NG (Fig. 3). Cultures of *K. oxytoca* I-A, the most NG-tolerant strain, grew to a density of 204 K.U. in the presence of 3.96 mM nitroglycerin. *P. putida* II-C grew to a density of 330 K.U. in the presence of 3.08 mM nitroglycerin, whereas turbidities of *P. putida* I-B cultures decreased in the presence of greater than 1.32 mM NG. Depending on the strain, the six BAAP isolates grew uninhibited in cultures containing from 1.32 mM to 3.52 mM NG. However, the growth of *P. syringae* pathovar *syringae*, a bacterium presumably not previously exposed to NG, was inhibited by 0.44 mM nitroglycerin.

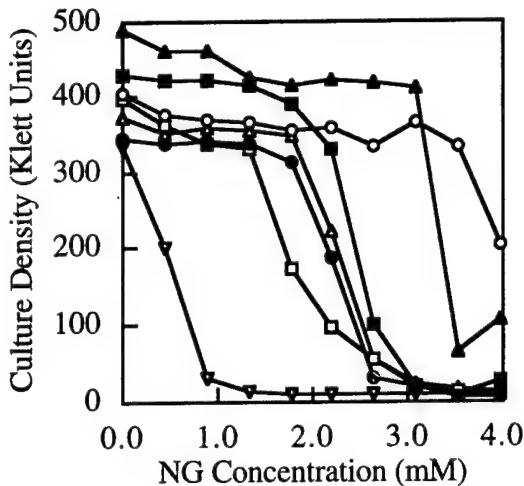


Figure 3. Culture densities attained by bacteria isolated at BAAP after 24 hours of incubation in the presence of NG. Each culture density reading is the average of two independent experiments. \circ , *K. oxytoca* I-A; \bullet , *P. fluorescens* II-A; \square , *P. putida* I-B; \blacksquare , *P. putida* II-B; Δ , *P. fluorescens* I-C; \blacktriangle , *P. putida* II-C; \blacktriangledown , *P. syringae* pathovar *syringae*.

CONCLUSIONS

Through our efforts to isolate and characterize nitroglycerin-degrading bacteria, we have noted that different strains of bacteria denitrify NG with varying regioselectivities. Nitroglycerin is comprised of a three-carbon backbone, with nitrate groups bonded to the C1, C2, and C3 positions. As a consequence of this structure, 1,2-dinitroglycerin can be formed by denitrification at the C1 or the C3 positions, while 1,3-dinitroglycerin can only be formed by denitrification at the C2 position. If enzymes catalyzing the removal of nitrite lacked regioselectivity, cleavage would occur randomly at all three positions, forming 1,3-DNG/1,2-DNG with a ratio of 0.5 (19). As reported, NG-denitrification enzymes employed by *P. putida* I-B exhibited regioselectivity, preferentially denitrifying nitroglycerin at the C2 position. Conversely, *P. putida* II-C randomly denitrified nitroglycerin. The different regioselectivities of these two strains suggests that among bacteria, different enzymes may be employed in the denitrification of nitroglycerin.

As shown in the NG-denitrification profiles for *P. putida* strains I-B and II-C presented in Fig. 1, these strains required different amounts of time to denitrify nitroglycerin to mononitroglycerin. *P. putida* II-C degraded almost all of the nitroglycerin present in its culture medium to isomers of DNG and MNG within four hours. Both isomers of dinitroglycerin, generated by NG degradation, were denitrified into MNG within approximately eight hours. Curiously, NG was completely degraded into MNG before the organism fully entered the exponential phase of cellular growth. Within a similar time frame, *P. putida* I-B also denitrified NG into DNG before entering exponential growth. However, *P. putida* I-B did not denitrify DNG with the same efficiency as strain II-C. It is reported that isomers of dinitroglycerin exert as significant a toxicity on mice and rats as nitroglycerin (2). Assuming that dinitroglycerin also exerts a toxic effect on bacteria, *P. putida* I-B may not have achieved a high cell density as rapidly as *P. putida* II-C because it was not as effective in removing toxic DNG from its culture medium. While not all of the BAAP isolates degraded NG as efficiently as *P. putida* II-C, all six strains denitrified NG into DNG before they entered exponential growth (data not shown). In addition, based on the observation that nitroglycerin was denitrified more slowly in the absence of an alternate nitrogen source, it is likely that NG is not degraded as a

preferred source of carbon or nitrogen. Instead, NG degradation may be a detoxification response by the bacteria. This hypothesis is further supported by the observation that a bacterial strain inoculated into NG-containing medium undergoes a longer lag phase, during which NG is degraded, than the same strain inoculated into medium lacking nitroglycerin. The longer lag phase may be related to time required to degrade/detoxify nitroglycerin. Thus, rather than using nitroglycerin as a preferred growth substrate, the BAAP isolates may degrade NG to detoxify their environment, which then allows them to multiply if the nutritional conditions are appropriate.

The results of nitroglycerin toxicity experiments suggest that NG-degradation enzymes of the BAAP isolates may have adapted to degrade/detoxify elevated nitroglycerin concentrations. As shown in Fig. 3, all of the BAAP isolates, with the exception of *P. putida* I-B, attained culture densities of at least 315 K.U. in the presence of 1.76 mM NG. Conversely, *P. syringae* pathovar *syringae*, an organism that had not been previously exposed to NG, exhibited an inhibition of growth in the presence of 0.44 mM NG. In addition, we observed that fourteen laboratory strains of bacteria, presumably not previously exposed to NG, were able to degrade 0.44 mM nitroglycerin to varying extents (data not shown). However, growth of these strains was inhibited by NG concentrations greater than 0.44 mM. Although the ability to degrade nitroglycerin appears to be a relatively common bacterial trait, organisms routinely exposed to nitroglycerin may have adapted to better degrade/detoxify higher concentrations of NG than organisms not regularly encountering this compound.

From an evolutionary perspective, nitroglycerin is a recent soil contaminant at the Badger Army Ammunition Plant. Although NG has only been present in the environment at BAAP for approximately fifty years, bacteria capable of degrading nitroglycerin more efficiently than those not previously exposed to this compound were readily isolated from this site. Additional studies will be required to provide detailed descriptions of the mechanisms used by the BAAP isolates to denitrify nitroglycerin.

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RESULTS OF A FOUR-YEAR *IN SITU* BIOVENTING DEMONSTRATION

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ABSTRACT

During early February of 1990, a ruptured pipe at a Burlington Northern Railroad (BNRR) fueling pumphouse in Alliance, Nebraska resulted in over 60,000 gallons of No. 2 diesel fuel spilling onto the surrounding soil. Several months later, a subsurface investigation indicated that soils were contaminated to a depth of over 65 feet below ground surface (bgs) and were in a position to impact groundwater, which was observed approximately 70 feet bgs. State regulatory agencies requested that BNRR develop and implement a remedial action plan to treat these diesel-contaminated soils and protect local groundwater. Parsons Engineering Science, Inc. (Parsons ES) was retained for this work and, after evaluating a variety of remediation technologies, recommended using soil bioventing methods to begin the removal of volatile benzene, toluene, ethylbenzene, and xylenes (BTEX) compounds and the long-term biodegradation of all fuel residuals.

Parsons ES first designed and implemented a bioventing pilot test to determine soil properties such as air permeability, and to assess the potential for both volatilization and long-term biodegradation of diesel fuel residuals at the site. Pilot test results confirmed that bioventing was feasible for the remediation of this site, and a full-scale bioventing system was installed on the site in September 1991. This system has operated continuously for over 4 years. BNRR personnel have been responsible for weekly system checks, and Parsons ES has been responsible for semi-annual respiration testing and for soil sampling to determine the level of cleanup achieved during the first 4 years of *in situ* bioventing. This document summarizes the work completed to date and the 4-year findings of this innovative technology demonstration.

1.0 SITE DESCRIPTION

The site is located south of a diesel fuel pumphouse, where the pipe rupture occurred (Figure 1). An estimated 15,000 cubic yards of soil has been contaminated to a depth of approximately 70 feet bgs. In preparation for the pilot test, a single 4-inch-diameter vent well (VW) and six 2-inch-diameter vapor monitoring points (VMPs) were installed on the

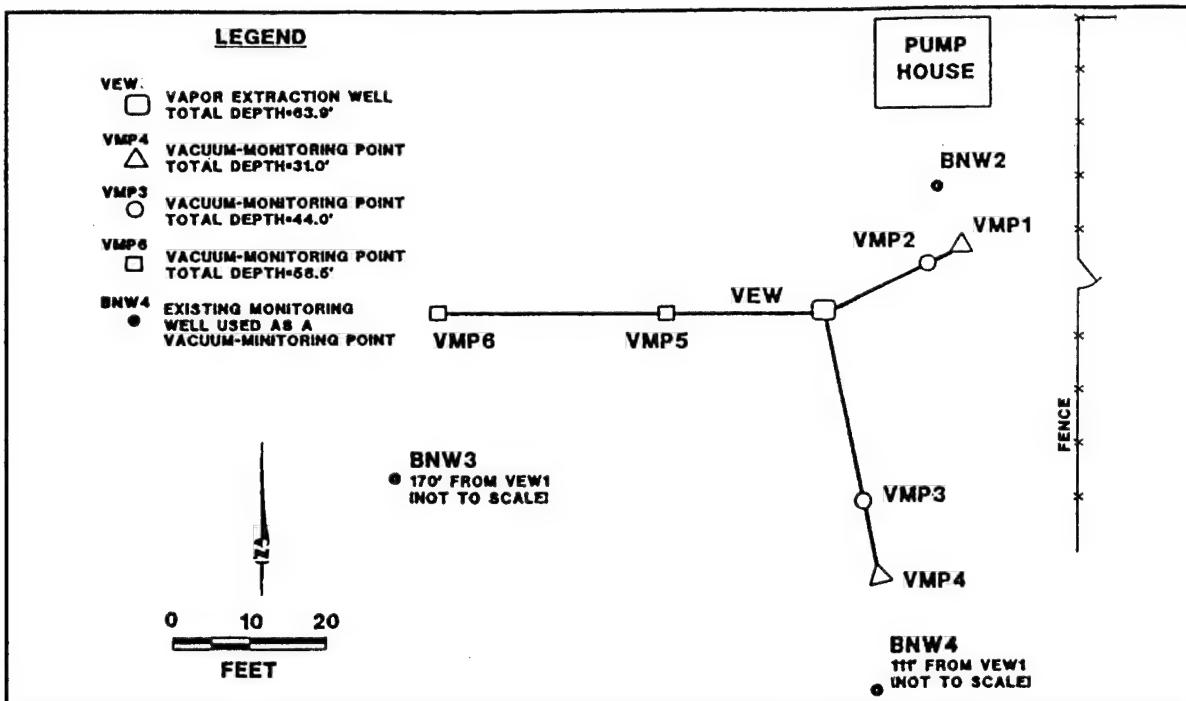


Figure 1. Site plan and monitoring point locations.

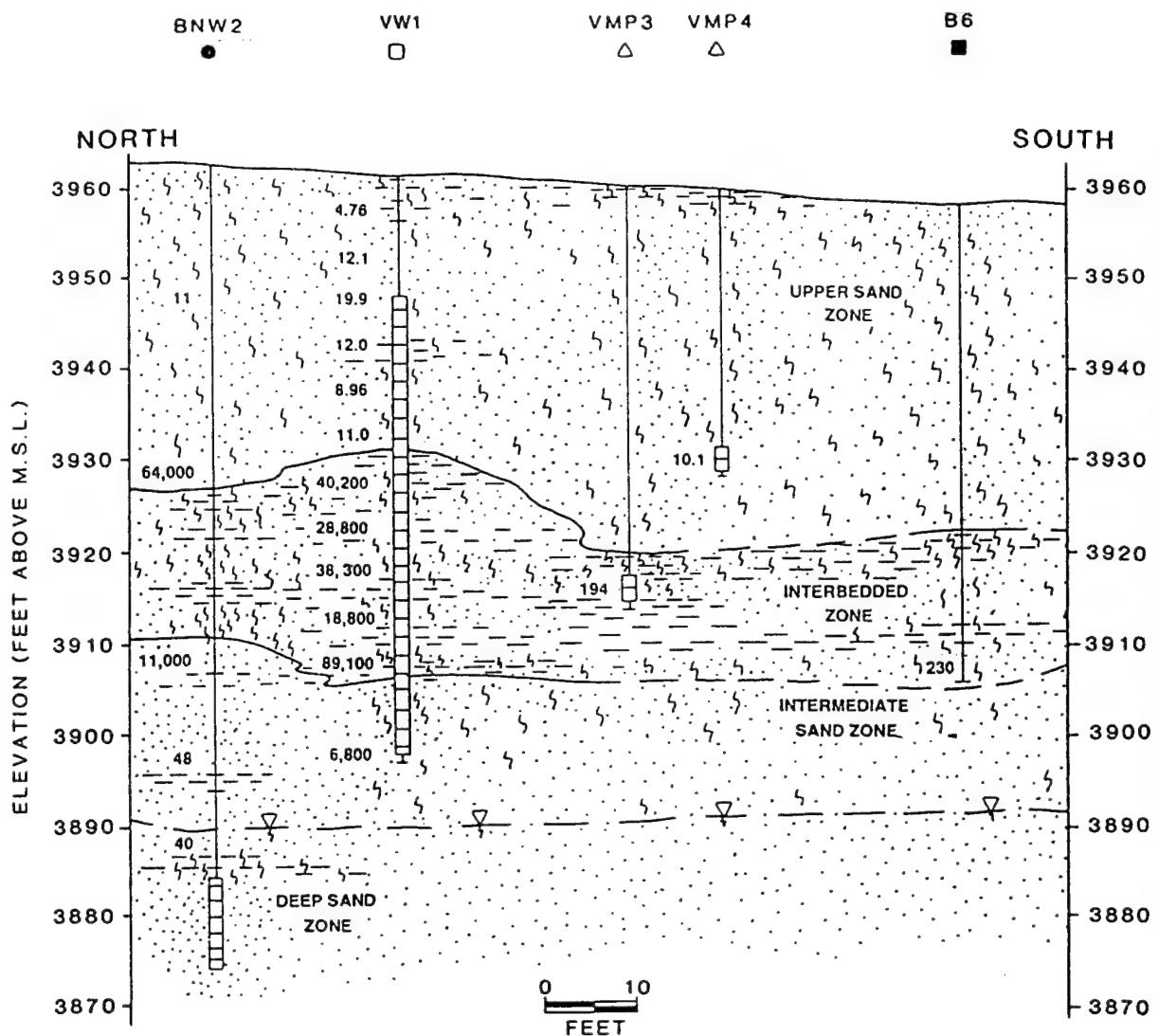
site. The Bioventing Pilot Test Results Report prepared for BNRR in June of 1991 presents the results of the pilot test and a more detailed description of the methods used to conduct the test.

1.1 Groundwater Conditions

Groundwater was observed at depths of 68 to 70 feet bgs. Dilute levels of BTEX compounds have been detected in groundwater beneath the site; however, only benzene and total petroleum hydrocarbon (TPH) concentrations exceed their respective cleanup levels of 5 micrograms per liter (ug/L) and 2 milligrams per liter (mg/L), respectively. Due to the thick column of soil above the water table, the vast majority of the diesel fuel spill is adsorbed and occluded in these unsaturated soils. Without soil treatment, soluble BTEX compounds could continue to percolate downward toward the groundwater, creating a larger and more concentrated plume of hydrocarbon contamination.

1.2 Soil Conditions

Soils at this site were characterized during the construction of the VMPs and the VW in April 1991. The general lithology in this area, shown in Figure 2, consists of fine- to medium-grained silty sands from the ground surface to approximately 30 to 35 feet bgs (upper sand zone), interbedded sand and silt/clay lenses that extend from 35 to 50 feet bgs (interbedded zone) and another layer of fine- to medium-grained silty sand that extends to



LEGEND

VW1 VENT WELL
 □
 VMP3 VAPOR MONITORING POINT
 △
 BNW2 MONITORING WELL
 ●
 B6 SOIL BORING
 ■
 38,300 INITIAL SOIL TRPH CONCENTRATION
 (mg/kg) (SAMPLES COLLECTED IN APRIL 1991)
 — — — GROUND WATER ELEVATION
 - - - GEOLOGIC CONTACT, DASHED
 WHERE INFERRED
 □ SCREENED INTERVAL AND TOTAL
 DEPTH OF WELL

LEGEND

-  CLAY
-  SILT
-  CLAYEY SAND
-  SILTY SAND

FIGURE 2
GEOLOGIC SECTION
FULL-SCALE BIOVENTING
DEMONSTRATION
PUMPHOUSE SPILL SITE

Alliance, Nebraska

a depth of 70 to 75 feet bgs (intermediate sand zone). Soil moisture varied from 2 percent in the intermediate sand to 11 percent in the interbedded silts and clays.

Soil gas permeability was quantified through vacuum response tests conducted as part of the pilot test in April 1991. Vacuum response and oxygen concentrations were measured at the VMPs and nearby groundwater monitoring wells (Figure 1) while soil gas was being extracted from the VW using a 10-horsepower (hp) vacuum blower. The soil responded rapidly to the vapor extraction system, with measurable vacuum response and increases in oxygen concentrations occurring in all soil zones, including the interbedded silt/clay zone. Using test methods developed by Paul Johnson and others, the average soil gas permeability was estimated at 5 darcys. Because the contaminated soil zone was entirely oxygenated using only the pilot-scale VW, no additional VWs were required for full-scale coverage.

1.3 Initial Soil Contamination and Nutrient Availability

The diesel fuel contamination in the soil appears to be localized within a 60-foot radius of the pumphouse. Initial total recoverable petroleum hydrocarbon (TRPH) concentrations are plotted on the geologic section shown in Figure 2. Based on initial soil analysis and observations made during drilling, it appeared that diesel fuel migrated rapidly downward at the spill site until it encountered the interbedded sand and silt/clay zone at approximately 30 to 35 feet. At this depth, the fuel spread laterally and continued its downward movement through more permeable sand lenses in the interbedded layer.

Initial soil samples collected from the screened intervals of VMP4 and VMP5 were analyzed for ammonia- and nitrate-nitrogen, total Kjeldahl nitrogen (TKN), and water-soluble phosphates. These analyses were performed to determine the concentrations of naturally occurring nutrients available in the soils. Ammonia-nitrogen was found at concentrations of 204 parts per million (ppm) in the upper sand zone (VMP4) and 4.2 ppm in the intermediate sand zone (VMP5), while nitrate-nitrogen levels ranged from 4 ppm in the upper sands to 11 ppm in the intermediate sand zone. TKN levels were found to be 4 ppm in both sand zones. Water-soluble phosphate concentrations ranged from 177 ppm in the upper sands to nearly 6,000 ppm in the intermediate sands. The relatively low nitrogen concentrations found in these soils may be limiting biodegradation rates. To determine if nitrogen addition could improve natural biodegradation rates, an ammonium nitrate solution was added to several VMPs after several months of bioventing. The addition of the nutrient solution did not significantly accelerate fuel consumption rates.

2.0 REMEDIAL GOALS

The objective of this remediation project was to reduce the potential impact of soluable diesel components on local groundwater by removing BTEX from the soil. Removal of BTEX compounds was to be achieved through a combination of short-term soil vapor extraction and continuous bioventing. A secondary objective was to remediate this large site without disruption to existing rail lines or the fuel pumphouse where the spill occurred and to obtain regulatory closure for the lowest possible cost.

3.0 FULL-SCALE SYSTEM DESIGN AND OPERATION

Based on the air permeability and oxygen influence observed during the pilot test, an extraction rate of 100 standard cubic feet per minute (scfm) was selected for full-scale bioventing operations. A 7-horsepower regenerative blower system capable of producing this design flow rate was installed at the site, plumbed to the existing VW, started up, and optimized in September 1991. Soil gas extraction was selected over air injection due to the immediate need to remove volatile and soluble BTEX compounds from the soil before further groundwater contamination occurred. In December 1994, the system was switched to an injection mode and the flow rate was decreased to 60 scfm. This modification was made because much of the soluble BTEX had already been removed/biodegraded, and because bioventing systems require much less maintenance when they operate in an air injection mode. The six VMPs installed during the pilot test continue to be used to monitor pressure response and to ensure that aerobic conditions are maintained throughout the contaminated soil volume.

The full-scale bioventing system has operated continuously for over four years with minimum maintenance downtime. The monthly electrical cost for the system is estimated at approximately \$280.00. BNRR personnel have been responsible for weekly system checks and monthly blower filter changes.

4.0 LONG-TERM PERFORMANCE MONITORING

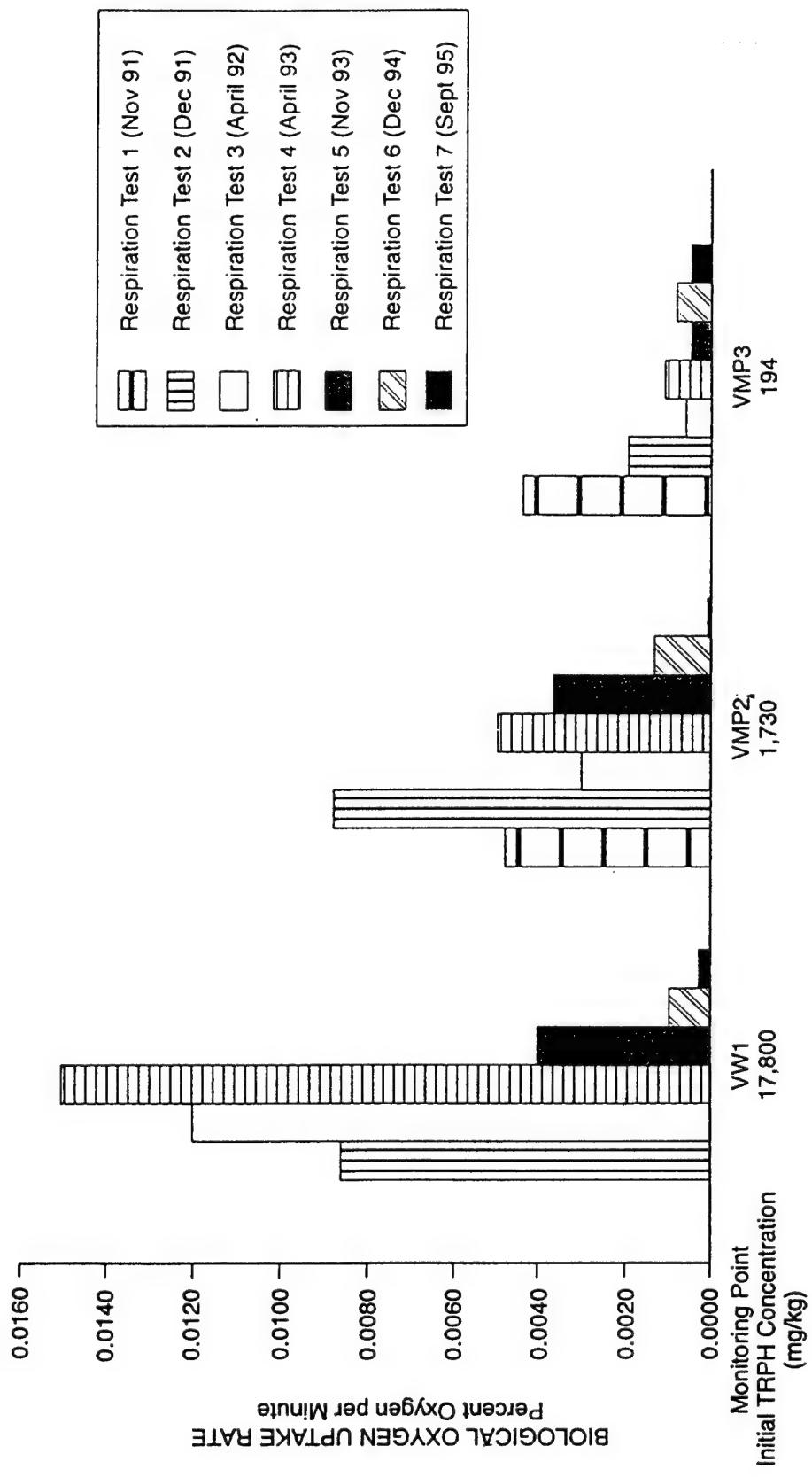
The fuel-consuming capability of native soil bacteria has been examined during seven *in situ* respiration tests conducted by Parsons ES over the four-year operation period. Emissions of volatile hydrocarbons to the atmosphere have been monitored to ensure regulatory compliance and to estimate the amount of hydrocarbons physically removed from the soil. Three soil sampling events, including the initial sampling event in April 1991, have also been conducted in order to document the removal/biodegradation of petroleum hydrocarbons at the pumphouse spill site.

4.1 *In Situ* Respiration Testing

Continuous air injection into contaminated soil zones provides the necessary oxygen for aerobic biodegradation. When the blower is turned off, oxygen is no longer delivered and soil bacteria consume the available oxygen. Oxygen consumption and carbon dioxide production were monitored at each VMP using a portable O₂/CO₂ gas analyzer. The rate at which soil bacteria consume oxygen is an important indicator of the viability of the fuel-degrading organisms in soils near each VMP. Uncontaminated background VMPs were also monitored during the initial respiration test. Oxygen levels at these background VMPs remained relatively constant at approximately 18 percent, indicating that biological oxygen consumption of natural (nonfuel) organic carbon and abiotic oxygen consumption were not significant in these soils.

The results of respiration tests at the VW and VMPs 2 and 3 are shown in Figure 3. Results indicate that the apparent rates of oxygen utilization have significantly decreased over time. Very low rates of respiration (less than 0.001 percent oxygen uptake per minute) had been measured in VMP3 during the last three tests, indicating that little fuel is now available for biodegradation near this monitoring point. Soil sampling at VMP3 in

FIGURE 3
 BIOLOGICAL OXYGEN UPTAKE DURING RESPIRATION TESTS
 FULL-SCALE BIOVENTING DEMONSTRATION
 PUMPHOUSE SPILL SITE
 ALLIANCE, NEBRASKA



September 1995 confirmed that TRPH levels have been reduced from 194 mg/kg to less than 3.3 mg/kg over 4 years of system operation. Respiration rates have also decreased significantly at VW1 and VMP2. Although TRPH concentrations are still somewhat high at fuel-impacted depths at these locations, respiration rates are minimal. Low respiration rates at VW1 and VMP2 indicate that the majority of the readily biodegradable fractions of the diesel fuel have been eliminated. The remaining TRPH in site soils is likely high molecular weight material, with corresponding low water solubilities.

Using a very conservative ratio of 3.5 pounds of oxygen for every 1 pound of hydrocarbon consumed, the fuel biodegradation rate can be estimated for soils immediately surrounding VW1 and each VMP. Using this estimation method, the average biodegradation rate at the center of the spill (near the VW) had been approximately 3,400 mg of TRPH degraded per kg of soil per year during the first two years of system operation (September 1991 to November 1993). During the final respiration testing event in September 1995, the average fuel hydrocarbon consumption rate was estimated to be 130 mg of TRPH degraded per kg of soil per year. This represents an order of magnitude decrease in the rate of fuel consumption, and indicates that the bioventing system has successfully accomplished its objective.

4.2 Volatilization

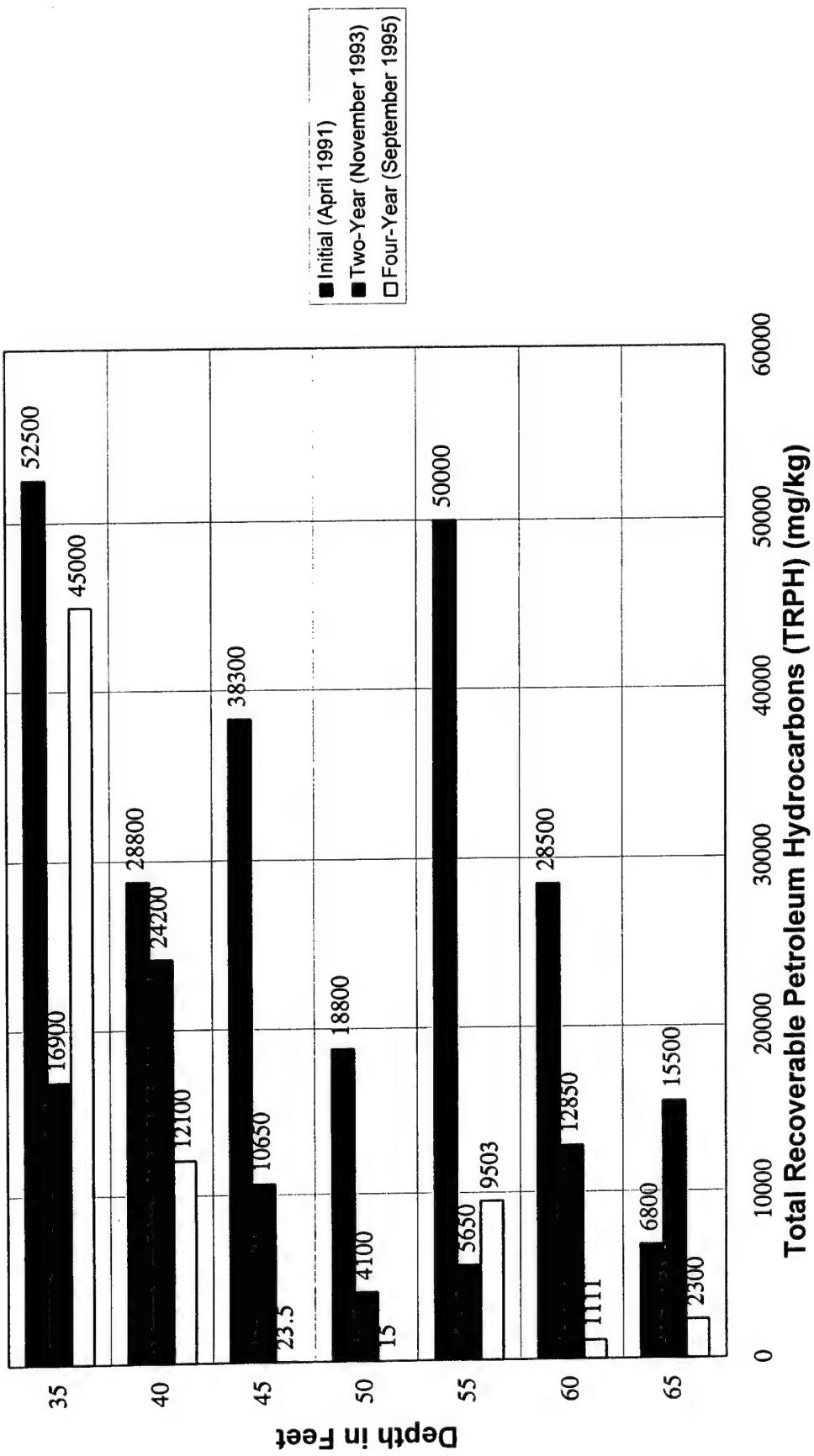
The removal of volatile and water-soluble compounds such as BTEX from this large diesel fuel spill was also a key objective of this remediation project. Regular sampling of extracted soil gas indicated that approximately 0.3 kg of BTEX and 14.7 kg of diesel vapors have been removed during each day of bioventing operation while the system operated in an extraction mode (September 1991 through December 1994). During this time, an estimated 21,400 kg of total volatile hydrocarbons were removed via extraction by the bioventing system. This mass of hydrocarbon removal could account for approximately 10,000 mg/kg reduction in soil TRPH.

4.3 Soil Sampling Results

In order to more accurately assess remediation progress, soil sampling programs were conducted in November 1993 and September 1995. In each sampling event, soil samples were collected from a number of boreholes located within a 20-foot radius of VW1. This area was selected for sampling because it represented the most contaminated portion of the site based on initial soil sampling. Sampling depths matched those of the initial site characterization in April 1991. A total of 18 samples was collected from four boreholes in September 1993, and 19 samples were collected from five boreholes in September 1995. All soil samples were analyzed for TRPH by Method 418.1, and six soil samples from each sampling event were also analyzed for BTEX by Method 8020. The samples which were also analyzed for BTEX compounds were chosen based on elevated field hydrocarbon analyzer readings.

Figure 4 illustrates the general reduction in diesel fuel concentrations from initial April 1991 levels. These soil sampling events indicate that an overall TRPH reduction of 75 percent has occurred over the past 4 years of bioventing. Only the 35-foot depth interval showed an apparent increase in fuel concentrations. This apparent increase is likely

FIGURE 4
FOUR-YEAR PETROLEUM HYDROCARBON REDUCTION
Full-Scale Bioventing Demonstration-Pumphouse Spill Site - Alliance, Nebraska



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Note: All two-year samples represent an average of 2 or more sample locations per depth.

caused by the non-uniform distribution of hydrocarbon contamination in the interbedded zone at this depth. Concentrations of fuel contamination are likely to be greater in clay lenses in the zone because of higher capillary retention of liquids, and because oxygen is more difficult to deliver in these soils. The soil sample collected during the September 1995 event could easily have contained a higher percentage of fine-grained soils than the sample collected during the November 1993 event, thereby yielding a higher fuel concentration.

The overall TRPH reduction observed during the first four years of system operation was approximately 75 percent. Fifty-five percent of the TRPH was removed in the first two years of system operation, with an additional 20 percent of the TRPH being removed between November 1993 and September 1995. These results indicate that the rate of TRPH removal is slowing over time, and that the benefits of continued system operation are decreasing over time.

Figure 5 illustrates the reduction in BTEX concentrations achieved during the last two years of system operation (from November 1993 to September 1995), and Table 1 summarizes the results of BTEX analyses for the September 1995 sampling event. Total BTEX concentrations have been reduced substantially at all depths, and BTEX concentrations overall have been reduced 75 percent between November 1993 and September 1995.

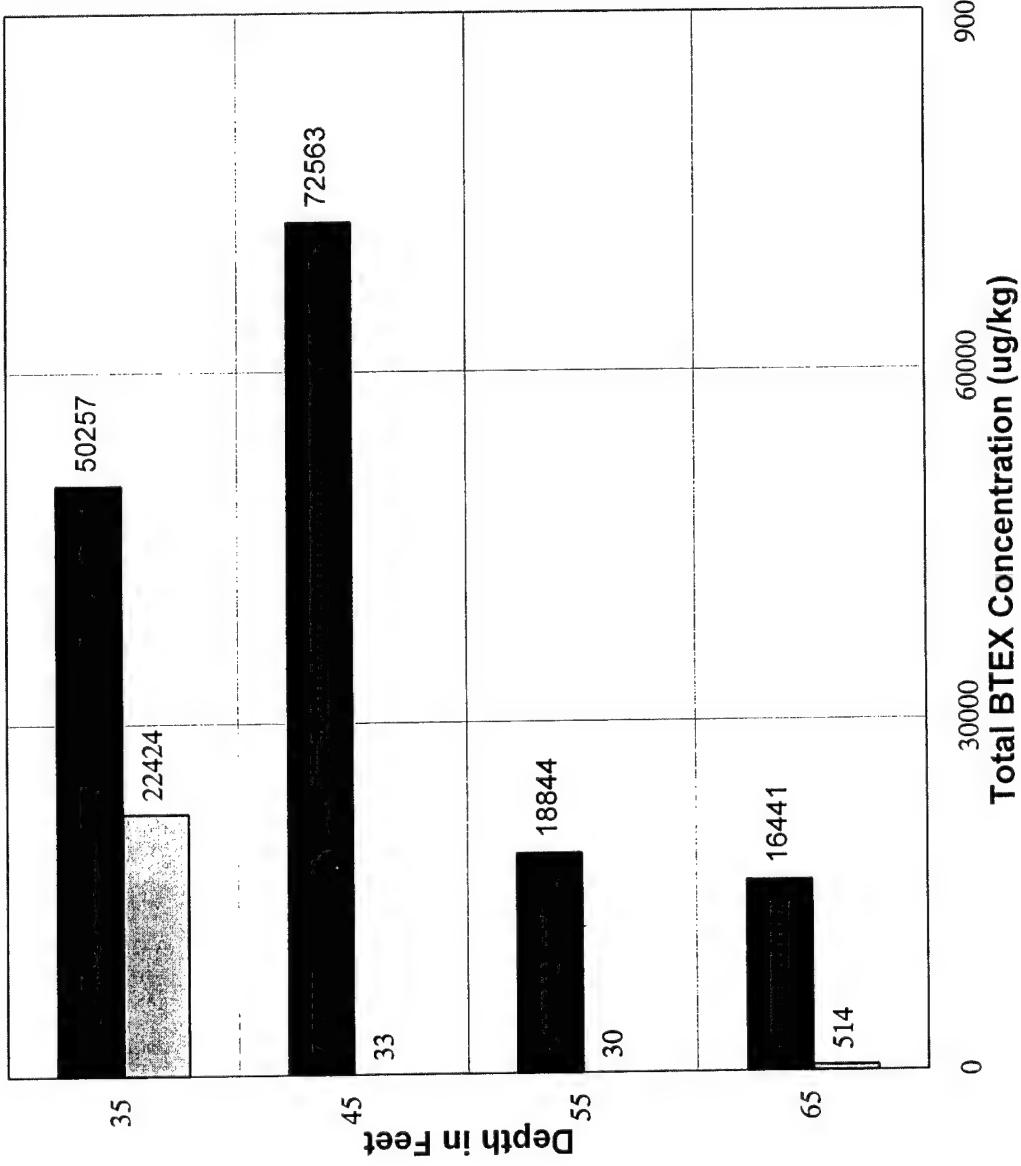
It is estimated that approximately 9,500 pounds of BTEX were spilled at the Alliance site in 1990. In November 1993, an estimated 1,630 pounds of BTEX remained in contaminated soil zones. As of September 1995, only 380 pounds of BTEX are estimated to be present in site soils. This remaining BTEX represents only 4 percent of the 9,500 pounds of BTEX initially released. Because 96 percent of the risk-driving BTEX compounds have been removed/biodegraded, the health risk at this site has been substantially reduced.

5.0 CONCLUSIONS

Full-scale bioventing at this large diesel spill site has produced encouraging results during the first 4 years of operation. Remediation is taking place throughout a 70-foot soil profile with no disruption to railroad operations or facilities. Specific indicators of progress include:

- Recent soil sampling results which indicated that a 75-percent decrease in TRPH concentrations has occurred in the most contaminated portion of the site during the 4-year demonstration. A 75 percent reduction in soil BTEX concentrations has also occurred in the last two years of system operation (between November 1993 and September 1995). The low levels of remaining BTEX should pose little or no risk to the local groundwater or to workers during any potential soil excavations at the site.
- Significant decreases in respiration rates across the site. These reductions in respiration rates indicate a significant reduction in the concentration of readily biodegradable, low- to medium-molecular weight petroleum hydrocarbons in fuel-impacted soils.

FIGURE 5
TOTAL BTEX REDUCTION IN THE LAST TWO YEARS OF SYSTEM OPERATION
Full-Scale Bioventing Demonstration - Pumphouse Spill Site - Alliance, Nebraska



022/722393/291.XLS

Note: Number of samples indicated in parentheses.

TABLE 1
 CONCENTRATIONS OF BENZENE, TOLUENE, ETHYLBENZENE, AND
 XYLEMES IN SOIL SAMPLES TAKEN WITHIN 20 FEET OF THE VENT WELL
 SEPTEMBER 1995

Sample I.D.	Depth (ft)	Concentrations in $\mu\text{g} / \text{kg}$			
		Benzene	Toluene	Ethylbenzene	Xylenes
BN-AL-SB8-65	65	ND	ND	ND	ND
BN-AL-SB8-35	35	140 J	300 J	550 J	27000
BN-AL-SB7-65	65	ND	ND	2.3 J	4.8 J
BN-AL-SB7-55	55	6.3 J	2.8 J	ND	ND
BN-AL-SB7-45	45	2.6 J	ND	ND	ND
BN-AL-SB7-35	35	88 J	270 J	1500	15000

J - Detected but value is estimated because it is below the practical quantitation limit.
 ND - Not detected.

5.1 Summary of Costs to Date

The total cost to date of bioventing at this site including pilot testing, full-scale installation, and 4 years of operation and maintenance is approximately \$146,000. Figure 6 shows a breakdown of total cost and a cost per cubic yard based on an estimated contaminated soil volume of 15,000 cubic yards. These costs include all Parsons ES project administration and reporting costs, but do not include electrical costs or BNRR labor costs for system checks. Parsons ES has completed this technology demonstration on time and within budget.

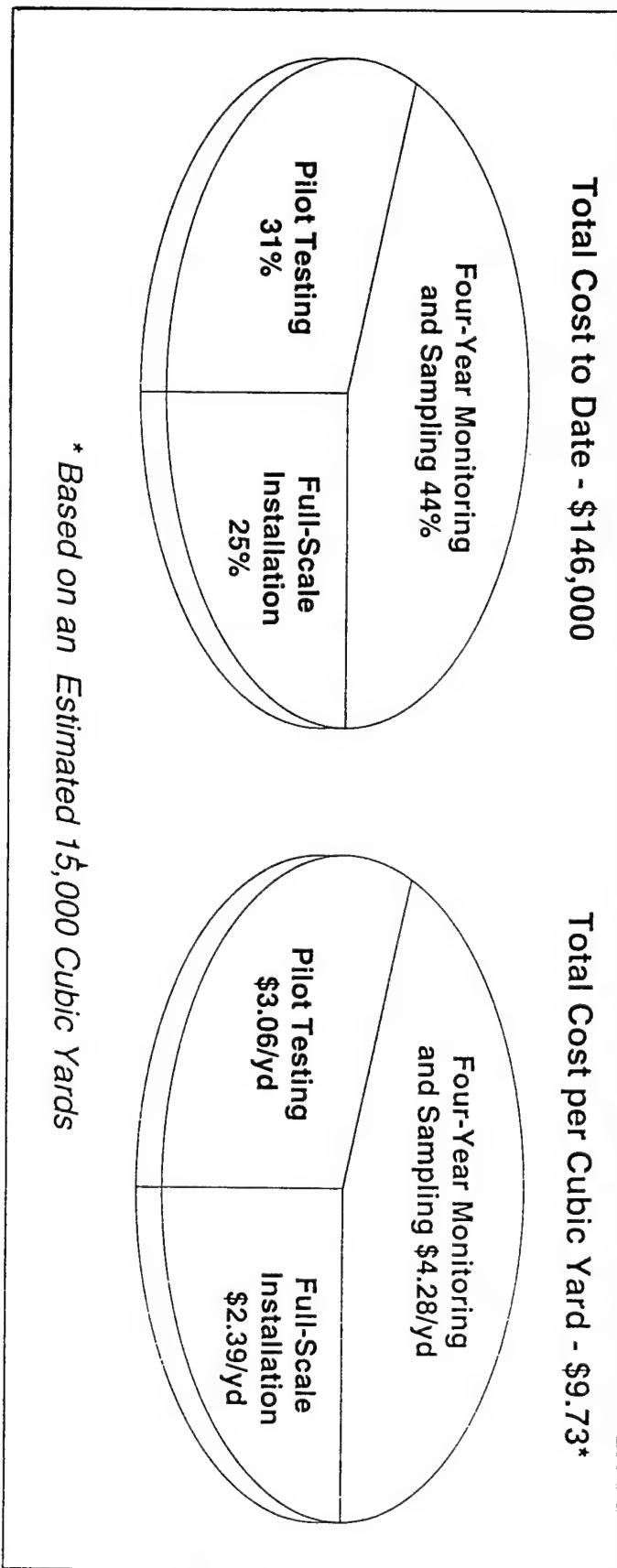
5.2 Site Closure

Because the majority of the volatile and water-soluble contaminants (i.e. BTEX compounds) have been volatilized and biodegraded, and because the high-molecular-weight compounds remaining in the soil are not expected to cause further deterioration of groundwater quality, Parsons ES recommended pursuing a risk-based closure of vadose zone soils at the pumphouse spill site. Early in 1996, the State of Nebraska reviewed soil data from the site and concurred that the site could be closed based on the significant risk reduction which had been achieved.

ACKNOWLEDGEMENTS

Parsons ES would like to thank Burlington Northern Railroad for their sponsorship of the full-scale bioventing demonstration and BNRR employees Mr. Joe Ringbauer and Mr. Pat Sherlock for their assistance in operating the system.

FIGURE 6
COST SUMMARY FOR
Full-Scale Bioventing Demonstration - Pumphouse Spill Site - Alliance, Nebraska



* Based on an Estimated 15,000 Cubic Yards

INNOVATIVE BIOLOGICAL SOLID-PHASE (OR LAND) TREATMENT OF PETROLEUM HYDROCARBONS (PHCs) AT THE UNITED STATES NAVY'S CRANEY ISLAND FUEL TERMINAL IN PORTSMOUTH, VIRGINIA

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ABSTRACT

Biological treatment was performed to remediate ~18,000 yd³ (14,000 m³) of petroleum hydrocarbon (PHC)-contaminated soil at a U.S. Navy land treatment facility. The soil was contaminated with Fuel Oil 535 which was a heavy, special grade fuel oil. The PHCs had weathered in place for 14 years prior to excavation and treatment. Most of the weathered product was contained in hard, hydrophobic clods up to several inches (centimeters) in diameter. Three innovative treatment areas (ITAs), i.e., ITA A (bacterial enzyme product), ITA B (selected bacterial mixture), and ITA C (oleophilic nutrient/selected bacterial mixture), were evaluated for increasing the rate and extent of biological treatment of the PHCs. The efficacy of those innovations was compared to conventional, mineral nutrient-amended land treatment. The rate of treating the PHCs in ITA C was approximately twice that of the other areas. With greater than an 80% reduction in PHC concentration in ITA C after 90 days of treatment compared to 67% reductions in the other ITAs and in the conventional treatment area (CTA) after 120 days of treatment, the benefit of the oleophilic nutrient/selected bacterial mixture for remediation of PHC-contaminated soil was demonstrated.

INTRODUCTION

In 1993, the United States Navy constructed and first tested a 600 ft x 1,000 ft (180 x 300 m), 14-acre (5.6 hectare), solid-phase (or land) treatment facility at the Fleet and Industrial Supply Center (FISC), Craney Island Fuel Terminal in Portsmouth, Virginia. The facility was designed to biologically remediate large volumes of PHC-contaminated soils obtained from Craney Island and other nearby Navy facilities. In 1994, under the U.S. Navy's Atlantic Division's (LANTDIV) Contract N62470-93-3032, Delivery Order 0016, OHM Remediation Services Corp. was contracted to remediate approximately 18,000 yd³ (14,000 m³) of PHC-contaminated soil transported to the facility from Site 13 at the Navy's FISC, Yorktown Fuels Division, Yorktown, Virginia.

Soil at the Yorktown facility had become contaminated with Fuel Oil 535. This was a heavy, special grade fuel oil that had been produced for the Navy by ARCO Petroleum Products Company. PHCs from tank still bottoms had contaminated loamy sand soil at the facility, and the PHCs had weathered in place for 14 years prior to excavation and treatment. Most of the weathered product was contained in hard, hydrophobic clods up to several inches (centimeters) in diameter. As determined by USEPA Method 418.1 (Total Recoverable Petroleum Hydrocarbons, Spectrophotometric, Infrared), total PHC (TPH) concentration in the soil averaged 1,200 mg/kg. As specified in the Virginia Solid Waste Management Regulations, the cleanup level at the site was 50 mg/kg TPH. A risk-based treatment variance for industrial locations later established the cleanup level at 1,000 mg/kg TPH.

The project objectives were to reduce TPH concentration to 50 mg/kg in a 120-day treatment period and to compare the effectiveness of three innovative treatment products to conventional treatment methods by being able to detect a 20% or greater difference in treatment with 80% confidence. Innovative treatment areas (ITAs) A (bacterial enzyme), B (selected bacterial mixture), and C (oleophilic nutrient/selected bacterial mixture) were constructed at the facility to evaluate three innovative products for increasing the rate of biological treatment of the PHCs. The efficacy of these innovations was compared to a conventional solid-phase control (Area D) after 120 days of treatment.

FIELD IMPLEMENTATION

Solid-phase (or land) treatment of hazardous waste is a managed technology that involves the controlled treatment of a waste in the upper soil zone. This treatment technology relies on the dynamic physical, chemical, and biological processes that result in the biodegradation, immobilization, or transformation of a hazardous waste to an environmentally acceptable level. Solid-phase treatment has been widely used throughout the world to treat petroleum industry and other industry wastes to acceptable levels.

In the 14-acre (5.6 hectare) treatment cell, the 18,000 yd³ (14,000 m³) of PHC-contaminated soil were spread to an average depth of 9.6 in (24 cm). ITAs A (bacterial enzyme), B (selected bacterial mixture), and C (oleophilic nutrient/selected bacterial mixture) were constructed at the facility to evaluate three products for increasing the rate of biological treatment of the PHCs. The efficacy of these innovations was compared to a conventional solid-phase control (Area D) after 120 days of treatment. Twelve tons (11 metric tons) of diammonium phosphate (DAP), (NH₄)₂HPO₄, was initially added to the soil in all areas of the treatment cell as an immediately available source of nitrogen and phosphorus to support microbial growth on the PHCs. On Days 30, 60, and 90, additional 12-ton (11 metric-ton) quantities of DAP were also added to the entire site. A schematic of the treatment cell is presented in Figure 1A. A Caterpillar SS-250 Soil Stabilizer and Reclaimer (Caterpillar, Inc.; Peoria, IL) and a Scat 482B Compost and Bioremediation Turner (Skat Engineering; Delhi, IA) were used to reduce the size of the clods, to mix the soil amendments, and to make the PHCs more available for aerobic biological treatment.

A sampling and analysis plan was developed which had the following objectives:

- To validate the attainment of the 50 mg/kg TPH cleanup level in soil at the site as required in the Virginia Solid Waste Management Regulations,
- To compare the effectiveness of three innovative treatment products to conventional treatment methods by being able to detect a 20% or greater difference in treatment with 80% confidence,
- To assure the maintenance of soil conditions conducive to enhanced microbial growth on PHCs, and
- To establish that leachate discharged from the treatment cell to the wastewater treatment plant at Craney Island would not adversely affect plant operations.

Samples were analyzed according to USEPA,¹⁻³ American Society of Agronomy/Soil Science Society of America (ASA/SSSA),⁴⁻⁵ and American Public Health Association's *Standard Methods* procedures (Table 1).⁶

With the exception of ITA C, baseline sampling was performed on Day 0 prior to startup of the treatment cell. Interim samples were collected on Days 30, 60, and 90, and final samples were collected from the treatment cell on Day 120. In ITA C, baseline sampling was performed on Day 30. Innovative treatment in Area C was, therefore, evaluated over a 90-day period. Baseline samples in each treatment area were collected along an equilateral triangular grid (Figure 1A) according to USEPA procedures.⁷⁻⁸ The maximum information from a fixed number of samples in a fixed area is obtained by maximizing the average distance between adjacent sample locations. The equilateral triangular grid affords the highest average spacing between sample locations and provides the maximum information about contaminant distribution.

TABLE 1. ANALYTICAL METHODS FOR MONITORING ANALYSES

Parameter	Analytical Method	
	Soil	Leachate
Total Petroleum Hydrocarbons (TPH)	USEPA 418.1	USEPA SW-846 M8015
Benzene, Ethylbenzene, Toluene, and <i>o</i> -, <i>m</i> -, and <i>p</i> -Xylene (BETX)	USEPA SW-846 8020	USEPA SW-846 8020
Oil & Grease	¹ NA	USEPA 413.1
Total Organic Halogens (TOX)	USEPA SW-846 9022	USEPA 450.1
Total Organic Carbon (TOC)	USEPA SW-846 9060	USEPA 415.1
pH	ASA/SSSA 12-2.6	USEPA 150.1
Available Mineral Nutrients		
Ammonium-Nitrogen (NH ₄ -N)	ASA/SSSA 33-3/33-4	USEPA 350.2
Nitrate-Nitrite-Nitrogen (NO ₃ -NO ₂ -N)	ASA/SSSA 33-3/33-4	² USEPA 352.1
Phosphate-Phosphorus (PO ₄ -P)	ASA/SSSA 24-5.1/24-5.3	USEPA 365.2
Potassium (K)	ASA/SSSA 13-3.3.1.2/13-3.3.3	USEPA SW-846 6010
Aerobic Heterotrophic Bacterial Population Density	SM 9215 B	NA
Soil Moisture Content	ASA/SSSA 21-2.2	NA

¹NA = Not Analyzed²NO₃-N

For each sampling event, a total of 26 and 120 sampling points were respectively collected in each ITA and in the CTA. On Days 0 and 120, for every 2 samples collected within each ITA, one composite sample was prepared for a total of 13 composite samples. For every 6 samples collected within the CTA, one composite sample was prepared for a total of 20 composite samples. Two duplicate samples were also collected and analyzed for TPH. One duplicate sample was collected from the CTA, and a second duplicate sample was collected from one of the ITAs. On Days 30, 60, and 90, those numbers of composite samples were respectively reduced to 2 and 6. In addition to TPH, baseline samples were also analyzed for BETX, TOX, TOC, pH, available mineral nutrients, bacterial population density, and soil moisture content. When baseline sampling was completed on Day 0, the soil was placed into windrows (Figure 1B) and the sampling plan was modified. A more detailed discussion of sample collection, windrow construction, and monitoring of the treatment cell has been previously presented.⁹

RESULTS AND DISCUSSION

Performance data has indicated that biodegradation of most chemicals in soil can be modeled using a first-order reaction rate or a mixture of first-order rates. First-order kinetics generally apply where the available

concentration of the chemical being degraded is low relative to the biological activity in the soil.¹⁰ Biological treatment of TPH was modeled according to the following integrated form of the first-order model:

$$C(s,t) = C(s,0)e^{-k(s)t}$$

where,

$C(s,t)$ = average TPH concentration (mg/kg) in treatment area s at time t (days),

$C(s,0)$ = average TPH concentration (mg/kg) in treatment area s at time 0 (days),

$k(s)$ = first-order rate constant (day⁻¹) for area s ,

t = time (days), and

s = treatment area.

The first-order model was fit to the TPH data using the method of generalized linear interactive modeling (GLIM) for the purpose of estimating initial TPH concentrations and first-order rate constants for each area. GLIM models are a generalization of ordinary linear models that can incorporate several features often found in real modeling situations. A GLIM model, rather than ordinary nonlinear least squares regression, was required, because the error variance (i.e., variance of random deviations of observed concentrations from the "true" values) in TPH data was not constant but was an increasing function of average TPH concentration (Figure 2A). This phenomenon is quite common in environmental and other earth sciences data, particularly when the data is collected over a spatial domain, and is sometimes referred to as the "proportional effect."

Table 2 presents estimates of the contrasts in the first-order rates of treating the PHCs in the ITAs compared to the CTA control (Area D). Although the fitted first-order rate constants for ITAs A and B were slightly higher than that for the CTA, the differences were not statistically significant at the 0.01 level. The p -values for the rate differences for ITAs A and B were respectively 0.13 and 0.31. The rate contrast between ITA C and the CTA was highly significant ($p = 2.7 \times 10^{-6}$). Based on initial results, the model was refit by assuming the same rate of TPH degradation (but different initial TPH concentrations) for ITAs A and B as for the CTA. Random variation was modeled as having a distribution symmetric about 0 and a standard deviation proportional to the TPH concentrations predicted by the model. Studentized residuals from a GLIM model are ordinary residuals divided by the standard error of prediction and corrected for transformation bias. Studentized residuals from this model were plotted against model predictions for the purpose of assessing whether the error variance was correctly modeled and whether higher order model terms might be required (Figure 2B). Inspection of Figure 2B, indicated the absence of any trends which would indicate lack of fit. The studentized residuals were distributed symmetrically about the zero line, and their dispersion appeared to be independent of the predicted values.

Studentized residuals versus normal quantiles were plotted to assess the shape of the error distribution (Figure 2C). The studentized error distribution appeared to be symmetric (but not necessarily normal) except for the extreme tails which exhibited some skewness to the right. Extreme points on the plots in Figures 2B and 2C were labeled according to their corresponding area. Figures 2B and 2C, therefore, indicated that there were no patterns which would suggest that the model was deficient. The estimated first-order rate for ITA C was approximately twice that of the pooled estimate rate for ITAs A and B and for the CTA (Table 3). Test results for TPH and first-order model predictions with 95% confidence limits for ITAs A, B, and C and for CTA D as a function of time are respectively presented in Figure 3.

TABLE 2. COMPARISON OF FIRST-ORDER RATES OF BIOLOGICAL TREATMENT IN THE INNOVATIVE TREATMENT AREAS COMPARED TO CONVENTIONAL LAND TREATMENT (AREA D)

Treatment Area	Treatment	Difference in Rates (Day ⁻¹)	Standard Error	Z-Score	¹ p-Value
A	Bacterial enzyme	0.00206	0.00184	1.12	² 0.131
B	Inorganic/trace organic nutrient and selected bacterial strain mixture	0.00091	0.00184	0.496	² 0.310
C	Oleophilic nutrient/selected bacterial strain mixture	0.00989	0.00218	4.56	³ 0.000002744

¹Probability that an observed difference (or a greater difference) in first-order rates of biological treatment could occur by chance under the null hypothesis

Null hypothesis states there was not a significant difference in first-order rates of biological treatment between conventional (Area D) and innovative treatment areas

²First-order rates of biological treatment for Areas A and B not significantly different than for Area D

³First-order rate of biological treatment for Area C significantly greater than for Area D

TABLE 3. FIRST-ORDER RATES OF BIOLOGICAL TREATMENT IN THE INNOVATIVE AND CONVENTIONAL LAND TREATMENT AREAS

Treatment Area	Treatment	K (Day ⁻¹)	Standard Error	95% Lower Confidence Limit	95% Upper Confidence Limit
A	Bacterial enzyme	¹ 0.00928	0.000803	0.0077	0.0109
B	Inorganic/trace organic nutrient and selected bacterial strain mixture				
D	Conventional land treatment				
C	Oleophilic nutrient/selected bacterial strain mixture	² 0.0184	0.00146	0.0155	0.0213

¹GLIM model refit with common first-order rate of biological treatment for Areas A, B, and D and with different initial concentrations for each area retained in the model

$$\begin{array}{ll}
 \text{ITA A} & C_0 = 741 \text{ mg/kg} \\
 \text{ITA B} & C_0 = 802 \text{ mg/kg} \\
 \text{ITA C} & C_0 = 943 \text{ mg/kg} \\
 \text{CTA D} & C_0 = 1,220 \text{ mg/kg}
 \end{array}$$

²First-order rate of biological treatment of TPH in Area C twice that of the other areas

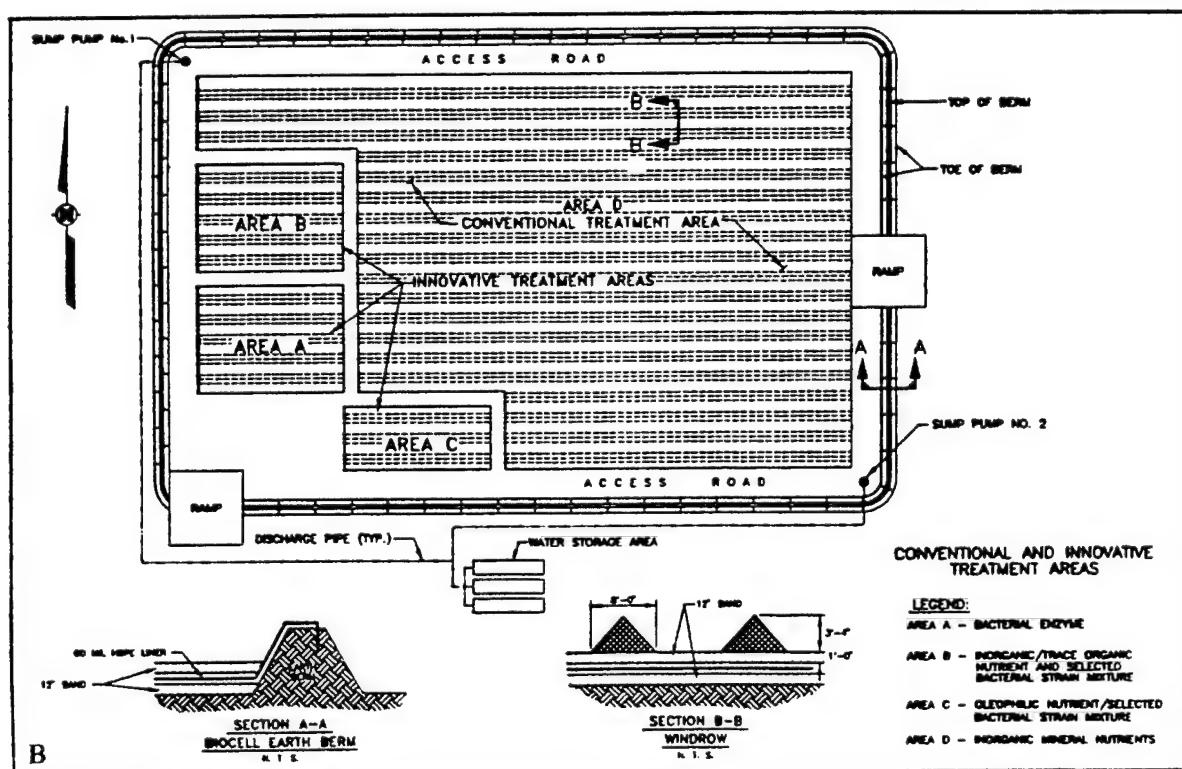
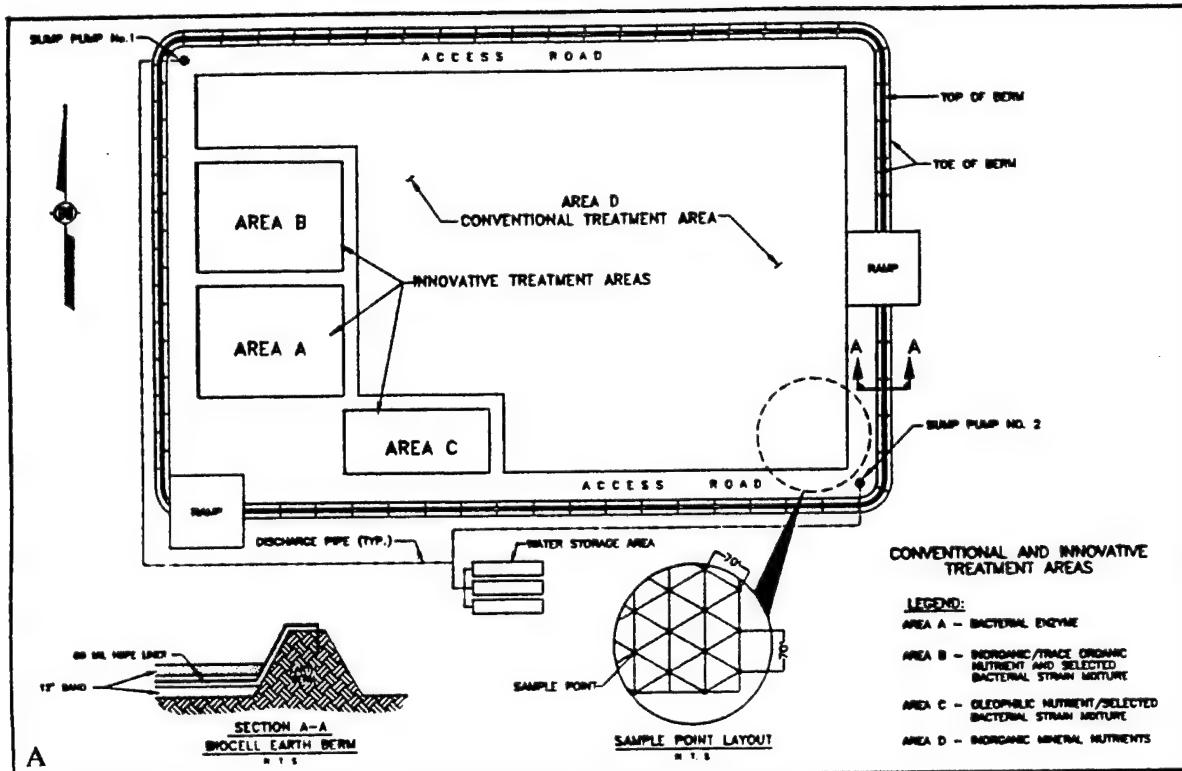


Figure 1. Land treatment cell and triangular grid sampling on Day 0 (A) and windrow construction for sampling on Days 30, 60, 90, and 120 (B).

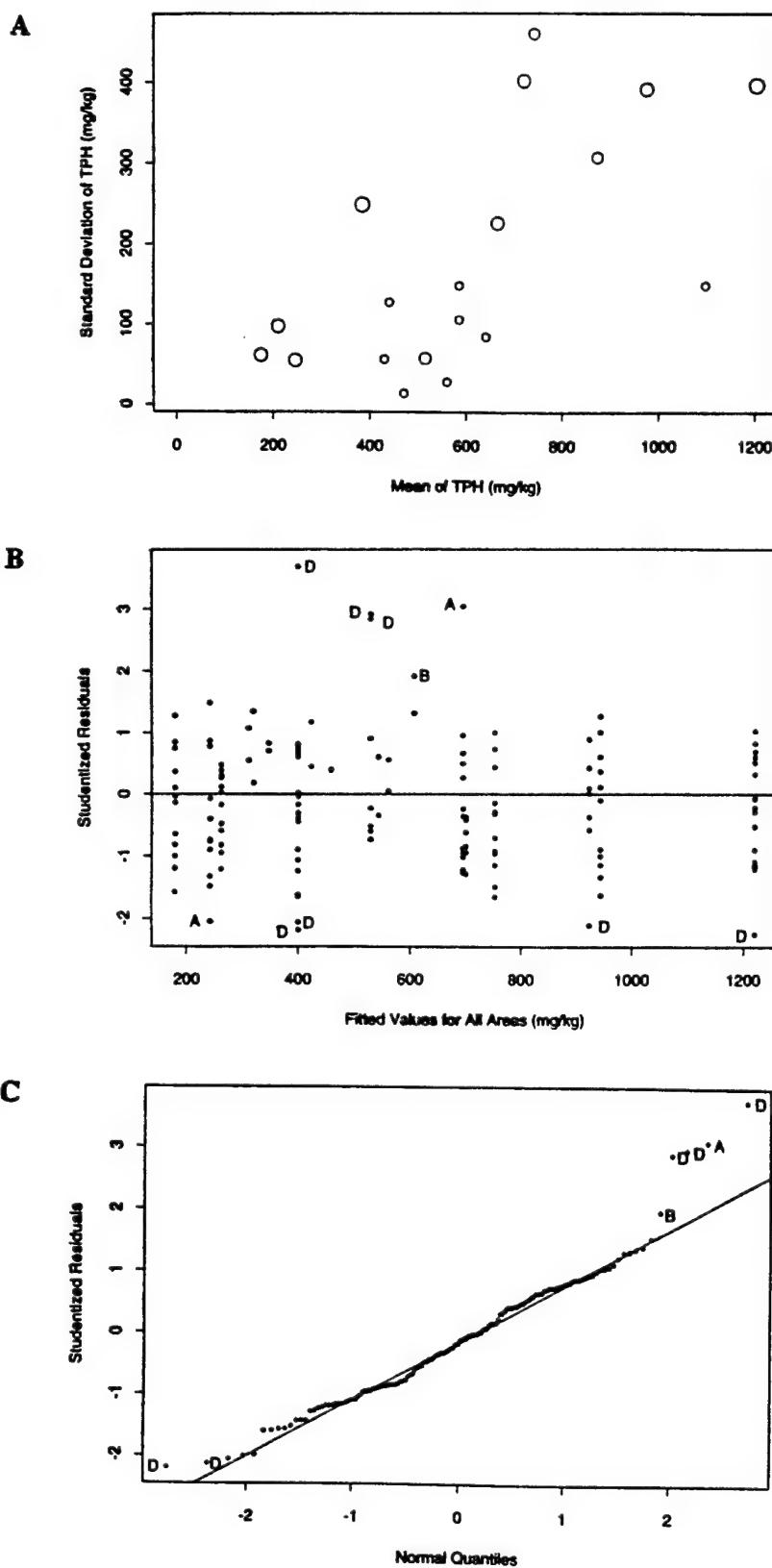


Figure 2. Diagnostic checking of the first-order model.

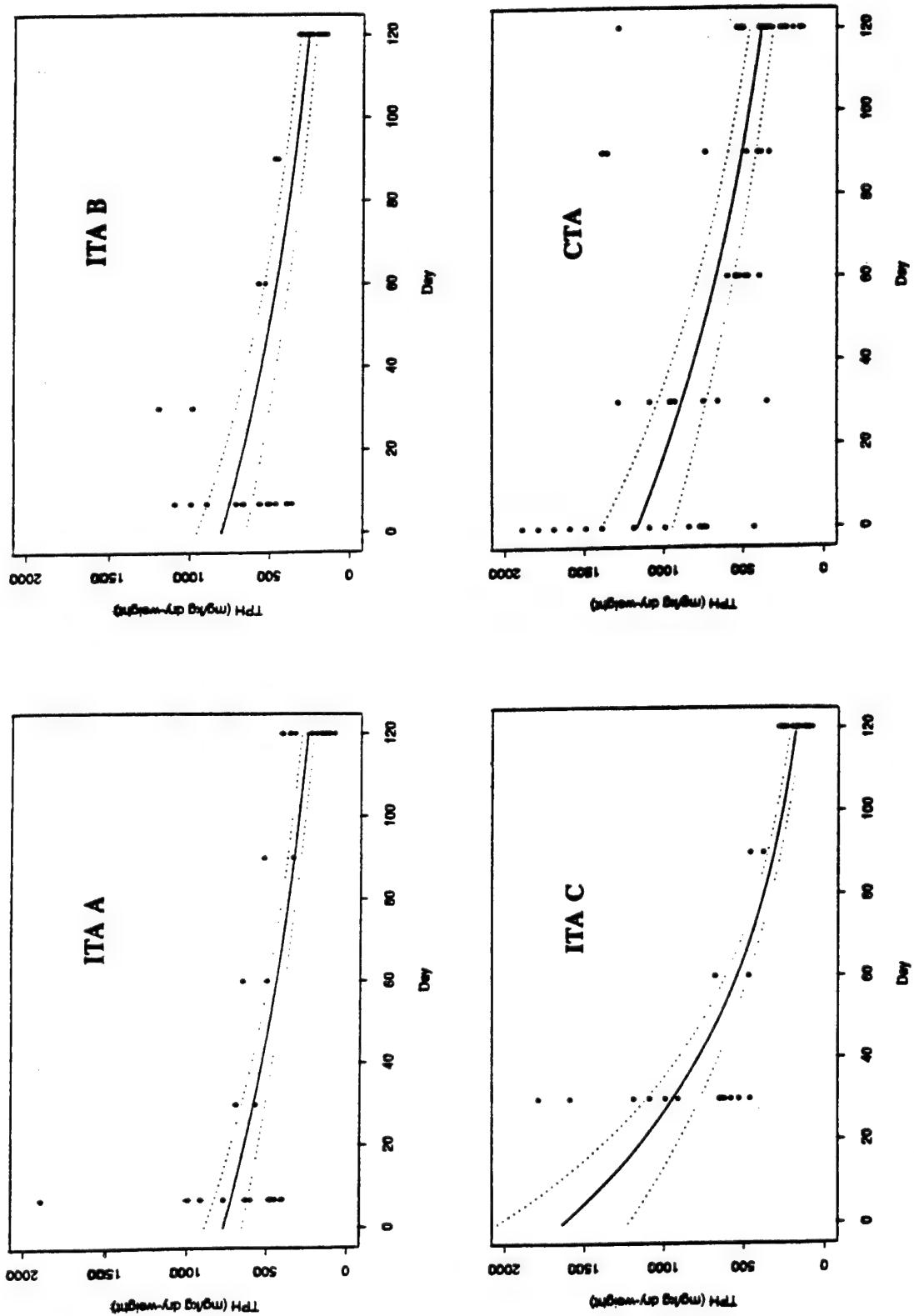


Figure 3. TPH concentrations and first-order model prediction with 95% confidence limits presented as a function of time for the ITAs and the CTA.

Table 4 presents the percent reduction for each area based on the final model and on the results of the initial and final sampling events. The extent of PHC treatment in ITA C was substantially greater than in any of the other areas. With greater than an 80% reduction in PHC concentration in ITA C after 90 days of treatment compared to 67% reductions in the other areas after 120 days of treatment, the benefit of the oleophilic nutrient/selected bacterial mixture for remediation of PHC-contaminated soil was demonstrated. The oleophilic nutrient / selected bacterial strain mixture evaluated in ITA C was developed by Eugene Rosenberg et al.¹¹ at Tel-Aviv University in Tel-Aviv, Israel through the financial support of Makhteshim Chemical Works Ltd (Beer-Sheva, Israel). The product, known as System E.T. 20 (formerly MCW.B 20) is listed on the USEPA's National Contingency Plan (NCP) Product Schedule.

TABLE 4. TPH REDUCTION IN THE INNOVATIVE AND CONVENTIONAL LAND TREATMENT AREAS

Treatment Area	Treatment	Treatment Time (Day Number)	Reduction in TPH (Percent)	
			Estimated From Initial and Final Data	Estimated From Model
A	Bacterial enzyme	0 to 120	69.7	67.1
B	Inorganic/trace organic nutrient and selected bacterial strain mixture	0 to 120	62.8	67.1
¹ C	Oleophilic nutrient/ selected bacterial strain mixture	30 to 120	80.8	80.9
D	Conventional land treatment	0 to 120	67.1	67.1

¹Substantially greater percent reduction in TPH concentration in Area C in only 75 percent of the time allowed for the other treatments

CONCLUSIONS

Innovative treatment in Area C (oleophilic nutrient / selected bacterial strain mixture) was more effective in treating TPH than innovative treatment in Areas A and B and conventional treatment in Area D. In ITA C, ~80% reduction in TPH was obtained over a 90 day treatment period (i.e., in only 75% of the time allowed for the other treatments). In Areas A, B, and D, ~67% reduction in TPH was obtained over a 120 day treatment period. The first-order rate of biological treatment of TPH in ITA C was about twice that obtained in the other areas. The effectiveness in treating TPH in ITAs A and B was not significantly different than in treating TPH in CTA D.

ACKNOWLEDGMENTS

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**RUSSELL ROAD LANDFILL
VIRGINIA'S FIRST SUBTITLE C LANDFILL CLOSURE**

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ABSTRACT

OHM Remediation Services Corp. (OHM), a wholly owned subsidiary of OHM Corporation, located in Richmond, Virginia under the Navy LANTDIV Multi-Contaminant Remedial Action Contract (RAC) is constructing a multi-layer composite cap over the 28-acre Russell Road Landfill at the Marine Corps Combat Development Command (MCCDC) in Quantico, Virginia. Completion of this project will mark the first closure of a Subtitle C (hazardous waste) landfill in the Commonwealth of Virginia. The composite cap layers from top to bottom are: topsoil, frost protection layer, filter/separation geotextile, stone drainage layer, cushion geotextile, 60-mil high-density polyethylene (HDPE) (both smooth and textured), Geosynthetic Clay Layer, and common subgrade.

Significant achievements during the course of the project included: Installation of sediment control structures that protected adjacent waterways and wetlands from 60 disturbed acres of construction activities; the acceptance by the Commonwealth of Virginia of value engineered changes to the Closure Plan and the cap design; "clean-closure" of seven areas adjacent to the cap; and the installation of 6,000 linear feet of leachate collection system averaging 20 feet below existing grade, and in some cases through 6 feet of bedrock. A large portion of the excavations were performed in Level B (supplied air) due to the unknown nature of the landfill subsurface.

The paper outlines the steps taken to successfully complete this design-build contract from site investigation through close-out report including a description of RAC processes emphasizing team built solutions between owner, contractor and regulators to maintain flexibility in the field. Additionally, the paper outlines the submittal and review process between the remedial contractor and the Virginia Department of Environmental Quality (VADEQ).

Detailed description of value engineered solutions include: Development of a 13-acre on-site borrow area; the identification of cap limits based on existing above-ground and subsurface conditions; and the use of geosynthetic clay liner in lieu of a 24-inch compacted clay layer, the redesign of a leachate collection system, and modification of project specifications to emphasize constructability of the cap.

1. INTRODUCTION

This paper describes work performed in the closure of the Russell Road Landfill. The project is being executed under the Naval Facilities Engineering Command's RAC awarded to OHM in 1993. This project was the 45th of the over 100 delivery orders issued to OHM to date, and at the time of the award was the largest undertaking of the RAC program. Prior to OHM's involvement, several years of study and design were performed, resulting in the selected remedy for this site. This paper is a case study in the closure process, from problem identification to execution of the remedy. The structure of the program is described as a framework for discussion on the execution methodology and technical decision-making that has led to a successful project.

2. RAC CONTRACT

The Russell Road Landfill project was awarded under the RAC. The RAC was specifically developed to conduct environmental cleanup and restoration projects at identified hazardous waste sites on Navy and Marine Corps installations, as well as other government sites. In this case, a Firm Fixed-Price contract was inappropriate since the project scope was not completely definable until work was already in progress. The program was selected as the contract mechanism since it is a Cost-Reimbursable/Award Fee contract, under which the Contractor is reimbursed for all reasonable costs incurred during the project. Contrary to the potentially adversarial relationship of a Firm-Fixed-Price contract, the RAC causes the contractor and the government to share risk. The award fee is used as an incentive for the Contractor to control costs while producing effective results. The Atlantic Division (LANTDIV) of the Naval Facilities Engineering Command (NAVFAC) awarded the multi-contaminant RAC to OHM based on their qualifications and experience in the remediation field.

There are many key personnel involved in each RAC Delivery Order. The main supervisor for the project is the Contractor. He is responsible for execution of a successful project in the field and for reporting accurate cost and schedule impacts on a regular basis to the Navy's representatives. In addition monthly updates are submitted to the Government which detail items such as progress in the field, re-work items, costs incurred, and predicted cost savings or over-runs, and Health and Safety statistics.

The Navy's on-base Resident Officer in Charge of Construction (ROICC) also has two representatives involved in the project: the Navy Technical Representative (NTR) and a Project Inspector. The NTR and the inspector are responsible for technical oversight of the project, and the enforcement of the contract plans and specifications. In addition, the NTR reviews the Contractor's monthly status reports and invoices, and provides input on the Contractor's award fee percentage at periodic intervals. Another important government representative is the Remedial Project Manager (RPM), who is usually located at the Engineering Field Division/Activity (EFD/EFA) level. He ensures compliance with Navy Policy, Guidance, and Environmental Laws and Regulations. He also provides technical input and obtains appropriate funding for the project.

The NTR and RPM report to the Contracting Officer's Technical Representative (COTR), also at the EFD/EFA level. The COTR has the chief responsibility for technical oversight of the contract. He also reviews the Contractor's status reports, monitors the project cost, and presents the award fee evaluation comments to the Technical Evaluation Board. Neither the NTR, the RPM, nor the COTR have the authority to change the cost or scope of the project. This responsibility lies with the Contracting Officer for the Delivery Order. If the project scope changes or if there is a significant increase or decrease in cost, the Contracting Officer will issue a modification to the delivery order accordingly.

3. AREA DESCRIPTION

The MCCDC is located within southern Prince William, northern Stafford, and eastern Fauquier Counties of Virginia, 35 miles south of Washington, D.C., and has an area of approximately 56,000 acres. The principal mission of the facility is training of Marine Corps and FBI personnel, and research, development, testing and evaluation of military hardware.

The base was activated in 1917, in time for World War I. The base has had major expansions that occurred during World War II, Korea, and Vietnam War Eras. The base is currently undergoing an increase in activity and personnel as a result of Base Realignment and Closure.

The base was proposed for the National Priorities List on May 10, 1993, and placed on the list on June 30, 1994. The base first submitted a notification of Hazardous Waste Activity on September 15, 1981. Quantico was first listed on the Hazardous Waste Compliance Docket in 1982. The base was granted Interim Status in 1983. The Department of Defense (DOD) Installation Restoration (IR) program began in 1984 with the completion of an Initial Assessment Study.

4. SITE DESCRIPTION

The landfill was established in 1960 and used for 22 years by all organizations on MCCDC. The areal extent is 28 acres, situated in roughly a triangle, with the base being approximately 1,100 feet and the length approximately 2,700 feet. The landfill is located along a former ridge that has been flattened, by landfill operations, into a plateau. The landfill was constructed via trench and fill methods, with two to four layers of trash being placed in the trench. Materials in the landfill include paint, waste oils, automobile batteries, photographic chemicals, construction debris, tires, scrap metal, petroleum contaminated soils, medical waste, and bituminous materials.

The landfill was originally closed in June 1983, under agreement with the State of Virginia. In December 1989, MCCDC was inspected by the Virginia Department of Waste Management. During the inspection, several violations were noticed, and a Notice of Violation was sent on April 12, 1990. As a result of negotiations between the State of Virginia and the Marine Corps, a Federal Facilities Compliance Agreement was signed in November 1991. This agreement stated that MCCDC would agree, among other things, to close four Resource Conservation and Recovery Act (RCRA) disposal units. One of the four units is the Russell Road Landfill.

5. BACKGROUND

In 1989, the Navy contracted with Ensafe, Allen and Hoshall to design the closure. The plan, approved in January 1995, called for a 2-foot layer of clay, 40-mil of very low-density polyethylene (VLDPE) liner, 1 foot of fine stone, and then 2 feet of common fill. The landfill was to be ringed by a 2-foot-wide, 20-foot-deep leachate collection trench that would gravity flow to two collection sumps. The limits of the landfill were determined by photo interpretation, and some magnetometer surveys.

The Navy contracted with OHM for the cap construction in February 1995. The team then began the constructability review process with the objective of developing detailed shop drawings. This led to design modifications that proved to reduce construction costs.

6. REGULATORY REQUIREMENTS

The landfill is a landfill as defined in Virginia Hazardous Waste Management Regulations (VHWMR) Part 2.102, or 40 Code of Federal Regulations (CFR) 260.10. The Closure Plan met all the requirements of VHWMR 672-10-1 Part X Section 10.13 and provided for a leachate collection system, a multi-layer cap, a gas vent system, and long-term maintenance.

Remedy selection was limited by the regulations to the types of capping material that would be used. Through partnership and communication with the VADEQ, several innovative materials and techniques were used.

7. PRE-CONSTRUCTION SITE INVESTIGATION

OHM and the Navy made a joint site inspection during May 1995. It was suspected at that time that the actual limits of waste appeared to exist outside the limits shown on construction drawings. The Closure Plan specified a leachate collection trench that would encompass all waste at an average depth of 20 feet below existing grade.

The system was specified to be a gravity system that discharged leachate to two sumps located at the southern end of the landfill. In order to develop a trench profile, an accurate location of waste limits and depth was critical.

Therefore, 126 test pits were dug on 100-foot centers around what was thought to be the perimeter of the trash placement area of the site. Pits were excavated from the existing treeline, outward or inward, until the visual extent of trash was located. The locations were then surveyed, and this data was used during the redesign effort. The limits were flagged and later surveyed.

As test pit information was gathered, it was discovered that waste extended much further to the south and in close proximity to a local road. Rather than backfilling the test pits then re-excavating approximately 30,000 cubic yards of waste, this waste was immediately relocated to within the landfill. When excavation was completed, the area was sampled and recommended for RCRA closure.

In addition to changes in the location of waste, the existing topography around the perimeter of the landfill varied from that shown on the construction drawings. A complete site survey was performed and the confirmed limits of waste were plotted. While mobilization activities were intensified and the installation of sediment control features was initiated, engineers were reviewing the results of the field investigation and beginning to create construction level drawings. With site preparation in full-swing, a revised Closure Plan was being modified for submission to the VADEQ.

8. DESIGN MODIFICATIONS

What started as the development of shop drawings and work plans grew to significant modification of the design. The changes were motivated by several factors: 1) the discovery of inconsistencies between maps showing existing conditions and current site topography; 2) the results of test pits excavated to determine the actual limits of waste; 3) the identification of potential borrow sources immediately adjacent to the landfill; 4) the successful use on Geosynthetic Clay Liners (GCLs) in lieu of clay on other projects; and 5) the need to develop a new profile for the leachate collection system, consistent with actual field conditions and vertical waste location.

Once it was determined that the incorporation of these changes would require a resubmission of the Closure Plan, the project team embarked on a complete and comprehensive modification to the design package. Significant changes made were: the replacement of 60-mil HDPE for 40-mil VLDPE; the replacement of two concrete leachate sumps with one double-walled HDPE leachate sump, a revision to the tie-in detail between the leachate trench liner and the cap liner; the replacement of 10-ounce geotextiles above and below the stone drainage layer, with 8- and 16-ounce, respectively; redesign of the leachate collection system; and perhaps most significantly, the identification of seven areas where, after waste would be removed from outside the proposed leachate trench and verification samples were returned, "clean closure" certification would be sought. Table 1 highlights the changes made and the benefits gained. Table 2 shows the design considerations necessitated by the changes.

New maps were generated and the project engineers began to design erosion control features that fit the actual site topography. The design utilized the rolling features of site to minimize earthmoving operations during the construction of basins and channels. Basins were formed by, wherever possible, construction of a berm/dike across an existing valley. Additionally, the structures had to be placed where they would not be a hindrance to any of the construction activities that were proposed (such as the leachate collection trench and the cap liner trench). Anticipating sediment flows from over 60 acres of disturbed land, OHM focussed on providing low maintenance structures and designed the structures to contain 150% to 200% of the required capacity. This ensured that in the event of a major storm event the basins would not overflow and would contain all the sediment and site runoff.

The installation of six sedimentation basins, one sediment trap, and over two miles of trenches and swales made up the majority of the 1995 work season. Utilizing as many natural features as possible, the total capacity for water retention was approximately 5,000,000 gallons. Moving berms constructed throughout the site diverted water away from open excavations, and the daily application of soil over exposed waste, prevented the migration of contamination of the site via surface water.

TABLE 1. CHANGES TO DESIGN

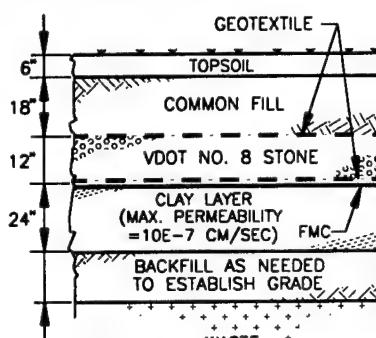
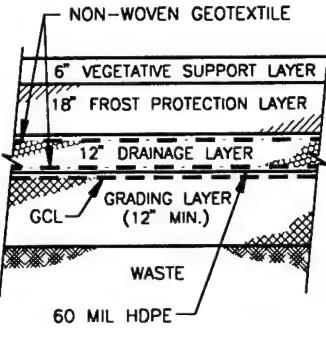
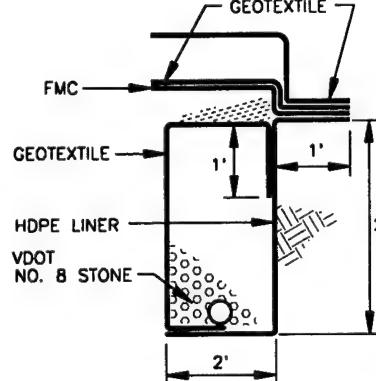
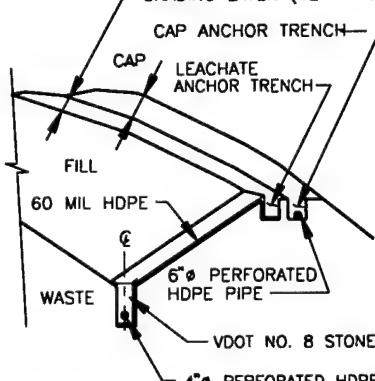
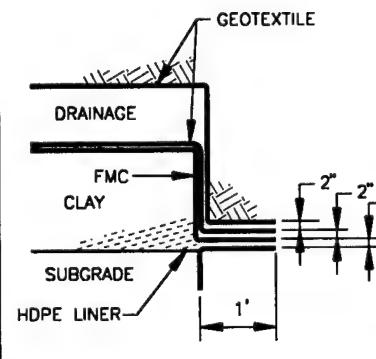
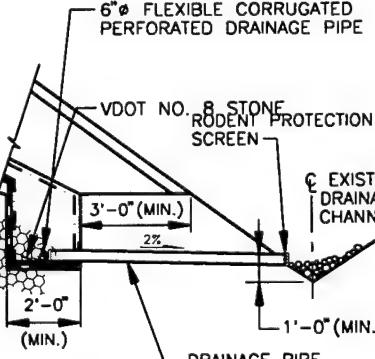
NEW CAP CROSS-SECTION		
ORIGINAL DESIGN	MODIFIED DESIGN	BENEFITS TO CHANGE
		<ol style="list-style-type: none"> 1) 10 oz. fabric was replaced with 8 oz. fabric. The fabric functions as a separation layer and filter layer. The materials are lower priced and are adequate for their function. 2) 10 oz. fabric was replaced with 16 oz. fabric. Heavy fabric was needed to withstand construction loads and to protect the liner. 3) 40 mil VLDPE was not available. The switch to 60 mil HDPE was motivated by questions of regulatory acceptance of 40 mil.
NEW LEACHATE TRENCH CROSS-SECTION		
ORIGINAL DESIGN	MODIFIED DESIGN	BENEFITS TO CHANGE
		<ol style="list-style-type: none"> 1) Liner trench separated to facilitate staged construction. 2) The excavation was benched to facilitate installation of the trench materials and for safety reasons. 3) Cleanouts were installed at 400 foot centers to allow for removal of any plugs within the collection system. 4) Placement of geotextile to prevent binding/clogging of the drainage. 5) The trench was redesigned to ease construction.
NEW ANCHOR TRENCH CROSS-SECTION		
ORIGINAL DESIGN	MODIFIED DESIGN	BENEFITS TO CHANGE
		<ol style="list-style-type: none"> 1) The drainage layer was keyed into the cap anchor trench. 2) Placement of lateral drains prevent blowouts of the trench. 3) Placement of geotextile to create a filter for the drainage stone, to prevent clogging. 4) Enhances long term stormwater management.

TABLE 1. CHANGES TO DESIGN (continued)

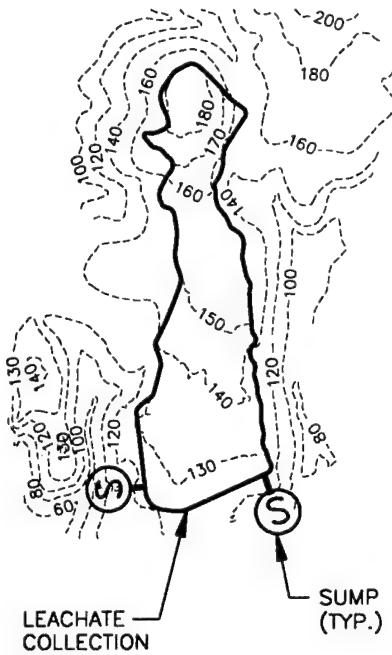
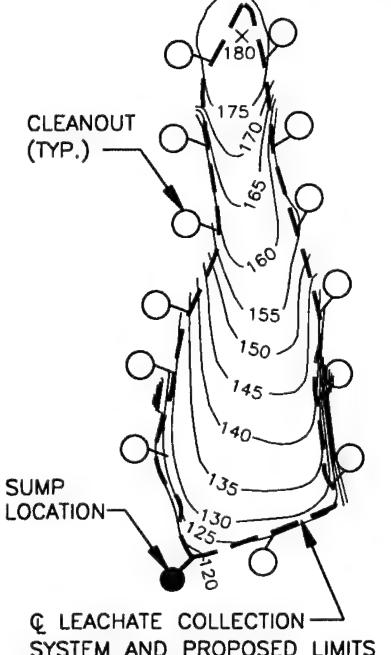
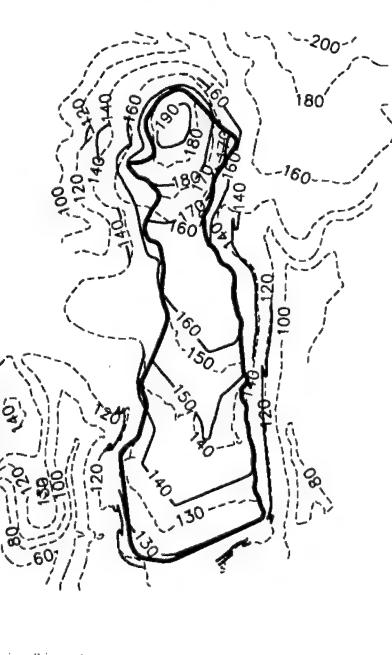
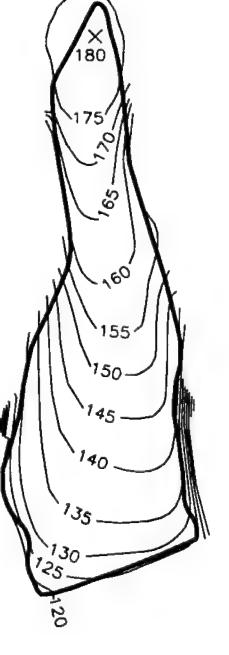
NEW LEACHATE TRENCH CROSS-SECTION		
ORIGINAL DESIGN	MODIFIED DESIGN	BENEFITS TO CHANGE
 <p>LEACHATE COLLECTION SYSTEM</p> <p>SUMP (TYP.)</p>	 <p>CLEANOUT (TYP.)</p> <p>SUMP LOCATION</p> <p>LEACHATE COLLECTION SYSTEM AND PROPOSED LIMITS OF RELOCATED/GRADED WASTE</p>	<ol style="list-style-type: none"> 1) Elimination of one sump. Single discharge/alarm. Elimination of one potential spill point. Placed to allow for easy access from paved road. 2) A concrete sump was replaced by a prefabricated HDPE sump. HDPE is a less expensive material and is more resistant to leachate breakdown. 3) Relocation of waste saved costs associated with extending the cap to encompass all of the waste fingers. 4) Cleanouts added.
REVISED GRADING		
ORIGINAL DESIGN	MODIFIED DESIGN	BENEFITS TO CHANGE
 <p>LEACHATE COLLECTION SYSTEM</p> <p>SUMP (TYP.)</p>	 <p>LEACHATE COLLECTION SYSTEM AND PROPOSED LIMITS OF RELOCATED/GRADED WASTE</p>	<ol style="list-style-type: none"> 1) Flow paths were shortened by reggrading the landfill. Shortened flow paths minimize potential blowouts in the cap anchor trench. 2) Increase in grade hastens the discharge of water and reduces the potential for infiltration, which could help induce a cap failure. 3) Grade adjustments allowed for better stormwater management, due to more water reaching the perimeter drainage channels, which then would be conveyed to the sediment control structures for final removal from the site.

TABLE 2. MODIFICATIONS AND ISSUES

Modification	Issues
1) GCL in lieu of Clay	<ol style="list-style-type: none"> 1) Verification of leachate production by running HELP Model. 2) Verify slope stability of all liner materials by performing direct shear testing. 3) Screen borrow soils to prevent damage to GCL fabric via penetration. 4) GCL minimizes the required QA/QC inspection and testing during installation
2) Eliminate Sump	<ol style="list-style-type: none"> 1) Capacity of single sump can contain 30 days of leachate generation. Based on HELP Model. 2) Longer flow path to sump requires change to pipe profile. 3) Placement of second sump would have been difficult if not totally impossible, do to site topography. 4) New waste depths allow for use of single sump. Do to change in condition and vertical location of waste from originally shown.
3) Fabric change from 10 oz. to 8 oz.	<ol style="list-style-type: none"> 1) Evaluate puncture resistance of fabric. 2) Evaluate shear strength due to settling. 3) 8 oz. fabric is normally used in separation layer. 4) 10 oz. fabric is not common and can require additional time to procure.
4) Fabric change from 10 oz. to 16 oz.	<ol style="list-style-type: none"> 1) Evaluate drainage properties of fabric. 2) Added puncture protection 3) 10 oz. fabric is not common. 4) 16 oz. fabric is a more common fabric weight for placement directly over HDPE.

9. LEACHATE TRENCH DESIGN

The results of test pits provided insight into the actual depth of waste within the landfill, as well as its lateral extent. It became apparent that the proposed grades for the leachate collection system would have to be modified to allow for the leachate collection system to function as originally designed. Additionally, concerns over the constructability of trench configuration were raised. It would be nearly impossible to construct a 24-inch-wide trench to a depth of 20 feet, place a HDPE geomembrane on one wall and a geotextile on the other wall, and then place a perforated HDPE pipe and backfill the excavation. There was no way to seam the HDPE liner sheets together to create the impermeable barrier that was intended in the design. With these concerns in mind, the trench was redesigned.

The most significant impact of the new design was the ability to successfully weld the HDPE liner sheets together. During the excavation of the trench, additional waste that was encountered within the excavation was relocated to within the footprint of the landfill, thereby removing any potential contamination from outside of the landfill.

During redesign of the leachate collection system, engineers proposed the elimination of one of the two leachate sumps. This proposal was based on a number of considerations. First, the regulations do not require any specific storage capacity for leachate collection. Second, the placement of a second sump was nearly impossible, due to the topography of the southeastern side of the landfill. Lastly, during the development of the trench profile, engineers were able to convey all collected leachate to a single collection point in the southwest corner of the landfill. This location was ideal because of its proximity to the site access way (facilitating maintenance) and its distance from other construction activity.

Leachate trench construction was initiated along the east border of the site. The final configuration of the trench was shown in Table 1. Included in the Closure Plan were four scenarios under which the leachate trench installation would progress for the possible subsurface conditions. For instance, provisions were made for cases where waste was encountered outside or below the designed leachate pipe invert.

The leachate trench was installed from the leachate sump in the south to the north. This allowed for the advancement of trench while leachate was collected in the system. Due to the severity of last winter, significant leachate flows were realized. Despite snow clearing activities from the landfill, over 500,000 gallons of leachate were generated. On-site treatment of leachate was not permitted, nor was reapplication of the leachate to the surface of the landfill. As a result, all leachate collected by the system was transported and disposed of off-site.

In addition to complications associated with leachate generation, fractured rock was encountered in the south trench at a depth of 10 feet. The presence of rock slowed installation of the HDPE sump, but was excavated with conventional earthmoving equipment.

10. WETLANDS

A local consultant was contracted to delineate the wetlands surrounding the property. Two streams border the east and west sides of the landfill. The impact to these streams was of paramount concern, both from the migration of sediment during construction and from the encroachment of proposed sediment control structures. The sediment basins were designed to minimize the impact to wetlands. As a result of the wetlands delineation, engineers could confirm that less than 1 acre of wetlands would be impacted. In addition to the environmental benefits realized, the quantity of wetlands impacted fell within the Corps of Engineer's Nationwide permit exemption, therefore obviating the need for an individual 404 Wetlands Permit.

11. BORROW AREA

OHM began an investigation to determine if a viable source of clay existed on site, and whether the available material could meet the project specifications and VADEQ regulations. After an exhaustive search of the site and the adjoining property, a potential borrow site was identified. Geotechnical testing was performed to classify the

soil and to determine its suitability for use as the clay barrier layer and to confirm that sufficient volume was available on site. Test pits were excavated within a 13-acre parcel of land located along the west side of the site. The results confirmed that, while the soil was not suitable for use as clay barrier material, it would be a sufficient quantity of material suitable for subgrade and frost protection soils. This discovery yielded a cost savings to the Navy and eliminated the need to import approximately 100,000 cubic yards of soil.

12. GEOSYNTHETIC CLAY LINER

During discussions with VADEQ, interest was expressed in the use of alternate products that would improve cap performance and save the government money. The VADEQ enthusiastically supported a proposal to substitute GCL for off-site clay. Potential savings were now quite significant since the search for an on-site source of clay was not successful. An equivalency review was performed to verify that the proposed GCL would meet all of the requirements of the clay. Additionally, a testing program was undertaken to determine strength parameters of the GCL and between each layer of the composite cap.

13. WASTE RELOCATION AND CLEAN CLOSURE

As previously mentioned a test pit investigation uncovered waste placement outside previously defined limits. Waste placement was determined to follow the landfill perimeter treeline in most cases. According to the original approved closure Plan for the project, no waste was to be relocated. Extending the cap limits to include these seven areas of waste outside the cap limits would increase its size by approximately 25% and would require the cap to extend over a local road.

Economic analysis demonstrated that the relocation of waste and subsequent "clean closure" of the relocation areas benefitted the project when compared to the prospect of extending leachate trench and cap around these areas. Clean closure of these areas being evaluated by comparison to background soils in accordance with SW846 criteria.

14. WASTE REGRADING

In addition to the movement of waste from outside the cap to within the landfill, waste was relocated within the landfill. The landfill was reshaped to an average 3% grade. Over 60,000 cubic yards of waste were moved within the landfill to achieve final waste grade. Above the regraded waste, a 12-inch grading layer will be applied as final subgrade. The final 6 inches of subgrade will be screened to insure that no soils in excess of 2 inches in diameter would be placed. This was a measure taken to ensure that the GCL would not be subject to puncture stresses.

15. ALTERNATIVE PRODUCTS

It is estimated that the use of a GCL in lieu of importing clay will save the project in excess of \$500,000. Factors contributing to this savings include material and installation costs that are lower than the delivered and installed costs of clay. In addition, the placement of GCL occurs immediately prior to geomembrane placement which mitigates the risks due to variations in weather inherent with clay placement. The VADEQ enthusiastically supported this alternative.

16. CONTRACT MANAGEMENT

With so many people involved in the administration of the RAC, teamwork is a necessity. Design build contracts require the simultaneous input from many interests. This project involved the NTR, RPM, Project Inspector, and a representative from Quantico's Natural Resources and Environmental Affairs Branch (NREAB). Weekly meetings with all government personnel guaranteed the best opportunity that all interests would be met. Frequent visits by the VADEQ assisted in plan development, but more importantly, established mutual trust and cultivated the working relationship.

CONCLUSIONS

Coordination with Regulators. The project team has developed an open relationship with the VADEQ. This relationship was fostered during the decision to modify the existing Closure Plan. A measure of confidence was established with the regulators that permitted the preliminary stages of construction to commence in advance of the approval of the revised Closure Plan. While a certain amount of risk is assumed, that risk is mitigated by understanding the regulators' objectives for the project. This could not happen without open and frequent communication.

While it is impossible to anticipate all field conditions, particularly during the excavation of a landfill, it was helpful to include a number of scenarios in the Closure Plan. The scenarios described proposed solutions under a number of different waste configurations. During the excavation of the leachate trench, the actual location and depth of waste would determine the quantity of excavation associated with the leachate collection system installation.

**EVALUATION OF A TRANSPORTABLE HOT-GAS DECONTAMINATION
SYSTEM FOR THE DECONTAMINATION OF EXPLOSIVES-CONTAMINATED
DEBRIS AND PIPING**

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INTRODUCTION

The manufacture, handling, and loading of explosives at Army industrial facilities have resulted in the contamination of process equipment such as piping, pumps, motors, powder boxes, and sewer systems. Because of this residual contamination, process equipment, piping and sewer lines cannot be reused or disposed as scrap without some sort of remedial treatment.

Over the years, the U.S. Army Environmental Center (USAEC) has investigated technologies that could be used effectively to treat explosives-contaminated materials. Using process equipment supplied by the government, pilot studies conducted at Hawthorne Army Ammunition Plant have shown that decontamination of explosives-contaminated structural components is possible. The process used a heated gas to thermally decompose or volatilize explosives with subsequent incineration in an afterburner.

Based on engineering data gathered during the Hawthorne pilot studies, WESTON, under contract to the United States Army Environmental Center (USAEC), was requested to design and supply a hot-gas decontamination system which is transportable and easily procured through commercial sources. The finished equipment was delivered to the Alabama Army Ammunition Plant (ALAAP) to conduct an equipment shakedown and validation testing using explosives-contaminated piping and oversized debris. The purpose of validation testing was to verify the effectiveness of the hot-gas process to remediate explosives-contaminated piping and debris to levels which would allow this material to be disposed of as scrap and to maintain at least a 99.99% destruction and removal efficiency (DRE) of contaminants out of the system afterburner. A total of nineteen (19) test runs were conducted during the validation testing period.

Testing activities conducted at the ALAAP with the hot-gas system, have demonstrated that the hot-gas technology can be used to support ongoing base decontamination operations and base closure activities where explosives contaminated piping, process equipment, and/or debris pose disposal nightmares.

BACKGROUND

The Department of Defense (DOD) owns a large inventory of materials that are contaminated with energetic compounds of explosives, propellants, or pyrotechnics, as a result of depot activities, ammunition plant manufacturing processes, and munitions demilitarization activities. As a matter of good management practice, these materials are routinely decontaminated using commonly used decontamination methods such as steam cleaning and fire.

Although steam cleaning effectively decontaminates the surfaces of contaminated materials to a 3X condition, contaminants may still be present in the surface voids or equipment internals. The 3X process also produces contaminated wastewater which must be treated before reuse or discharge. At present, there is no analytic method available which accurately determines the contaminant concentration left within the pores of materials which have been decontaminated to meet 3X criteria, however, in order for these materials to be released from government control to be landfilled, scraped, or reused the materials must meet 5X criteria.

By definition, 5X treatment assumes materials are thermally heated to a uniform temperature of 1,000°F for a minimum of 15 minutes. Fire is the most effective means currently used to decontaminate explosives- and energetic-contaminated materials to the 5X condition. In some instances this process is controlled by flashing contaminated materials within an enclosed oven, but more commonly the process is uncontrolled

and accomplished by open air burning and/or detonation. Since environmental regulations are becoming more rigorous every year, it's likely the practice of open burning and/or open detonation for decontamination of explosives-contaminated materials will be severely limited or disallowed because this process results in non-regulated air emissions. The flash ovens allows control of process off-gases, however, the process is essentially an incineration process which currently carries both negative public and regulatory agency perceptions. Finally, materials decontaminated using either open burning or flashing methods are usually not suitable for reuse and must be scrapped or landfilled.

Is there an alternative? Is there a process that not only successfully decontaminates explosives- and energetic-contaminated materials, but a process that achieves decontamination levels equal to 5X criteria? Is there a process whose emission levels can be monitored throughout the decontamination process? Is there an available process which has none of the negative connotations of incineration, but is still able to successfully decontaminate equipment so that the equipment could be reused following decontamination? USAEC's testing with the hot-gas process seems to meet these requirements.

Hot-Gas Decontamination (HGD) Technology History

USAEC has been conducting laboratory investigations and pilot-scale studies of the hot-gas process since 1978. Based on promising laboratory work with chemical warfare agents, a pilot-scale study using agent spiked samples was conducted at Dugway Proving Ground, Utah¹. This controlled pilot-scale study successfully demonstrated the ability of the hot-gas process to decontaminate agent from a concrete and steel structure.

To further evaluate the hot-gas process on agent, USAEC selected a mustard thaw pit at the Rocky Mountain Arsenal for a field demonstration of the hot-gas process². Three tanks (2-2,600 gallon and 1-250 gallon) were also left in the mustard pit during the field demonstration to test the effectiveness of the hot-gas process in decontaminating process equipment. This field demonstration once again proved the effectiveness of the hot-gas process. Mustard agent was successfully decontaminated from the concrete pit, contaminated steel tanks, and process off-gases.

Based on the successful pilot-study results at Dugway, USAEC determined to investigate the effectiveness of the hot-gas process on explosives-contaminated materials. Pilot-scale tests of the hot-gas process, using explosives-contamination, were conducted at the Cornhusker Army Ammunition Plant³. Results from the Cornhusker tests indicated that the hot-gas process seemed to be effective at treating explosives-contaminated materials. To verify this finding, USAEC contracted for additional hot-gas studies to be conducted at the Hawthorne Army Ammunition Plant^{4,5} using a flash chamber modified for the hot-gas process. Explosives-contaminated machinery, piping and metal debris such as shell casings were treated in one study, and explosives contained within munitions such as ship mines, depth bombs, and 106mm - 5 inch

¹ Pilot Plant Testing of Hot-Gas Building Decontamination Process; Task Order 1. Report No. AMXTH-TE-CR-87130. Prepared by Batelle Columbus Division. 30 October 1987.

² Final Technical Report, Field Demonstration of the Hot-Gas Decontamination System. Report No. SFIM-AEC-ET-CR-95011. Prepared by Batelle Pacific Northwest Laboratories, Parsons Engineering Science, Inc., and Batelle Columbus Operations. February 1995.

³ Pilot Plant Testing of Caustic Spray Hot-Gas Building Decontamination Process; Task Order 5. Report No. AMXTH-TE-CR-87112. Prepared by Arthur D. Little, Inc. August 1987.

⁴ Task Order - 2: Pilot Test of Hot Gas Decontamination of Explosives-Contaminated Equipment at Hawthorne Army Ammunition Plant (HWAAP) Hawthorne, Nevada. Report No. CETHA-TE-CR-90036. July 1990. Prepared by Roy F. Weston, Inc. July 1990.

⁵ Demonstration Results of Hot Gas Decontamination For Explosives at Hawthorne Army Depot. Report No. SFIM-AEC-ET-CR-95031. Prepared by The Tennessee Valley Authority Environmental Research Center. September 1995.

projectiles were treated in a second series of tests. The results from these studies verified the effectiveness of the hot-gas process in treating explosives-contaminated materials, but indicated that equipment enhancements would be required to optimize the process.

Hot-Gas Decontamination System Equipment Design Criteria

At both Cornhusker and Hawthorne, modified equipment proved the basic validity of the treatment process, but post test recommendations indicated that better system efficiencies and process optimization could be achieved using equipment specifically designed for the hot-gas decontamination concept.

Starting with these recommendations as a baseline, USAEC contracted WESTON to design and procure hot-gas decontamination system equipment which could meet the following equipment criteria:

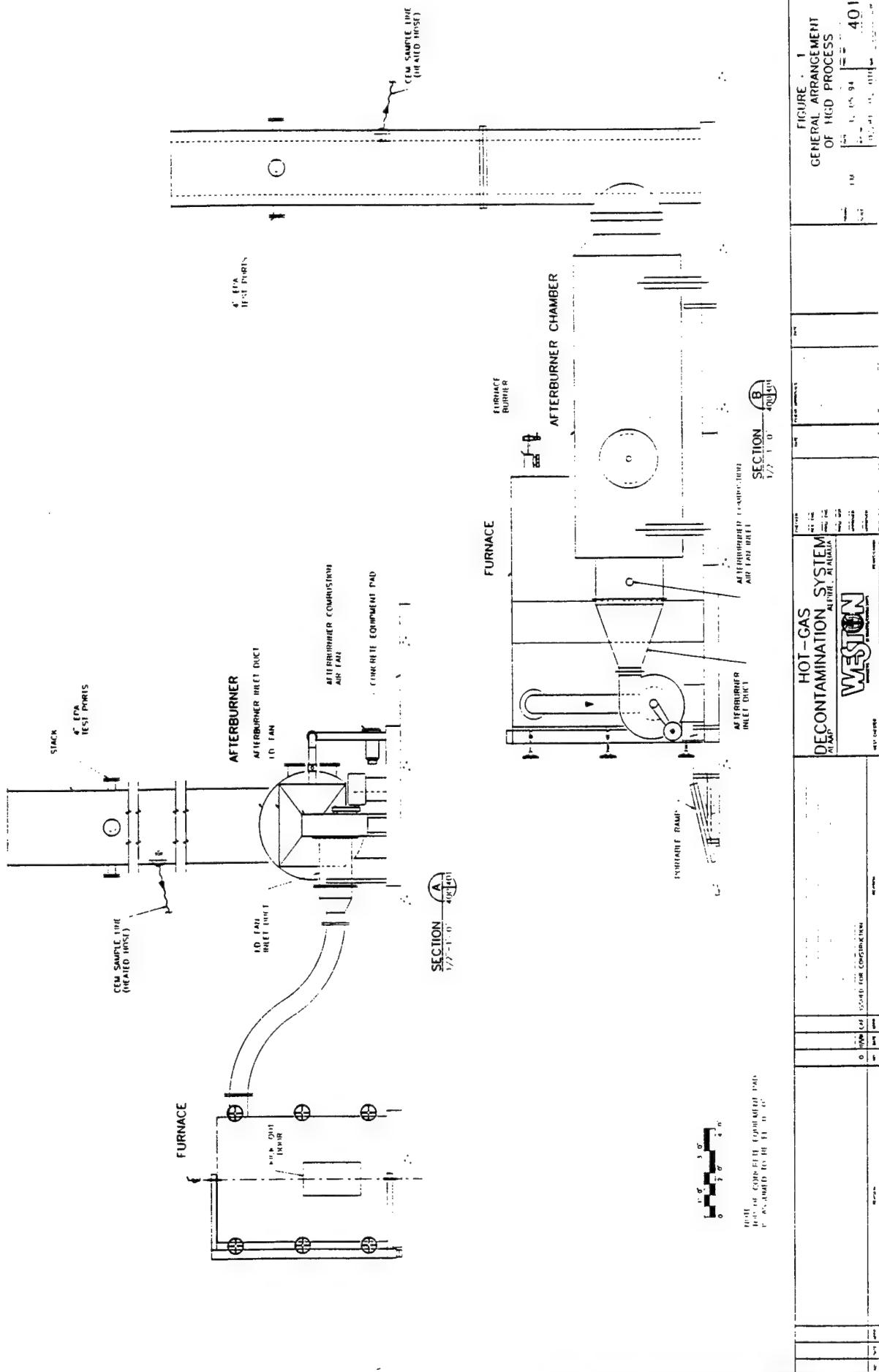
- Design a system which could be procured easily from commercial sources. "Custom" equipment designs were discouraged.
- Size the equipment so that it could be transported easily from site-to-site.
- Design a system which could be operated either locally at the equipment or remotely from a control room to ensure operator safety.
- Design process equipment which minimized system leakage.
- Provide system equipment which could reach treatment temperatures quickly and maintain treatment temperatures once operations began.

The Selected Hot-Gas Decontamination System Design

Based on the noted design criteria, the general arrangement for the second generation hot-gas equipment design which was supplied to USAEC is shown in Figure 1. The hot-gas equipment which was delivered to USAEC's Alabama Army Ammunition Plant (ALAAP) hot-gas site is a skid-mounted, easily transportable unit which consists of four basic elements: the hot-gas furnace, the system ID Fan, the afterburner, and stack. The hot-gas equipment furnished operates on a batch basis and is controlled remotely from two (2) remote control panels. The unit can also be operated locally to support system maintenance activities.

The hot-gas furnace was supplied by L&L Special Furnace Co., Inc. of Aston, PA. The furnace is a propane-fired, box-type furnace with an integrated ceramic fiber-lining. The furnace is rated for a total heat release of 1 million Btu per hour. Depending on the load size and material composition of the load, the furnace can easily maintain material temperatures up to 700°F. The furnace skid is approximately 17 feet long by 7 feet wide.

The system Induced Draft (ID) Fan is mounted downstream of the furnace on the afterburner skid and is used to maintain a negative draft between the furnace and afterburner. The fan was furnished by Chicago Blower, supplied with a variable speed drive, and rated for 2,250 cfm at 650°F. The fan has also been



equipped with vibration sensors and over-temperature sensors to alarm when furnace off-gases reach temperatures in excess of 700°F.

The afterburner equipment and stack were furnished by Arretech Environmental Systems, Inc. of Tulsa, Oklahoma. The afterburner is propane-fired and rated for a total heat release of 2.45 million Btu per hour. The afterburner is capable of thermally treating approximately 3,400 LB/hr of contaminated off-gases from the hot-gas furnace at a treatment temperature of 1,800°F with a minimum residence time of 2 seconds. The afterburner skid is approximately 28 feet long by 6 feet wide. The system stack, which is located at the discharge end of the afterburner, is approximately 23 feet high with a 29 inch inside diameter. The stack is equipped with 8 sample port locations to support emissions testing. The stack is disassembled from the skid and laid on its side to support shipment.

The afterburner and furnace systems were each supplied with a local and remote control panel. The local panels are located on each respective skids. The remote control panels for each system were located approximately 750 feet away from the hot-gas equipment, in a control room trailer. All system equipment can be started and stopped from either the local or remote panels. Both furnace and afterburner systems are equipped with individual temperature and burner controls. System interlocks, which create interdependency between the systems, have been installed to prevent startup or continued operation of the equipment when either a safety or operational condition exists which would require system shutdown.

Because of the small system footprint and height of the system, the hot-gas equipment can be easily transported over the road. It is unlikely that special permitting would be required to ship the system. Skid mounting allows for "pick and place" setup of the equipment once a suitable area has been prepared. We suggest allowing 2 days for equipment placement. For testing at ALAAP, the hot-gas equipment was placed on a curbed, concrete pad. The site was supplied with 480-volt electrical service, and a 5,000 gallon capacity propane tank to supply system propane. No system water is required.

Purpose and Objective of Validation Testing at Alabama (ALAAP)

Although pilot-scale studies have shown the hot-gas decontamination process to be effective in treating explosives- and agent-contaminated materials, potential users still have questions about the technology. Of primary concern:

- What are the costs associated with a full scale application
- Will the technology work on "my" specific explosives-contamination profile without creating other environmental hazards?

To address these concerns, USAEC contracted WESTON to conduct validation tests of the hot-gas equipment illustrated by Figure 1. The objectives of the hot-gas process validation tests were to evaluate the operability of the equipment and to determine:

- The effectiveness of the hot-gas process on various explosive-contaminated items such as: metal, clay pipe, and contaminated debris.
- The destruction and removal efficiency (DRE) of the hot-gas process using clean metal, clay pipe, and debris (cinder block) spiked with 2,4,6-trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX) and 2,4,6-trinitrophenylmethylnitramine (Tetryl).

- The time and temperature relationships for the decontamination of explosives on metal, clay and block surfaces.
- The optimum treatment time and temperature required for the complete destruction and removal of explosives and their breakdown components .
- Gather air emissions data on the hot-gas process to support future permitting of the process and equipment.

To meet these objectives a test plan was developed ⁶. The test plan was reviewed and approved by USAEC. Permission to conduct testing was also required from the Alabama Department of Environmental Management (ADEM).

TEST PLAN and TREATMENT CRITERIA

To meet the test objectives a total of 15 validation test runs, as illustrated by the test matrix provided in Table 1, were planned . Treatment temperatures ranged from 300°F to 650°F depending on the test run. A combination of clean metal pipe, clean clay pipe, and clean cinder block were spiked with an explosives-paste mixture which contained either TNT, RDX, or Tetryl. Twelve of the 15 test runs , as indicated by the (D) on the matrix, also treated contaminated debris from the ALAAP remediation effort. A spike mixture contained only 1explosives-type and was not mixed with other explosives-spike mixtures on the same test plate. Once the hot-gas furnace reached the desired treatment temperature, soak times (or hold time) were varied from 0 - 12 hours soak time depending on the test run.

TABLE 1
VALIDATION TEST MATRIX

Temperature	300°F	400°F	500°F	550°F	600°F
No Soak					Test #9, #16A, 16B, #16C
1 hour Soak	Test #12	Test #11	Test #13	Test #10	Test #7, #14, #15
2 hour Soak			Test #8		Test #6
4 hour Soak			Test #3 (E)		Test #5
6 hour Soak		Test #2 (E)	Test #4		
12 hour Soak			Test #1 (E)		

(E) Indicates furnace discharge gas and emissions testing was conducted during these test runs.

Confirmatory sampling and analysis was conducted before and after treatment using EPA Methods SW8460 and 8330. The 8330 analysis uses an HPLC to analyze for the 9 explosives and explosives-breakdown components listed below.

⁶ Draft Treatability Study Test Plan for the Evaluation of a Transportable Hot-Gas Decontamination System for the Decontamination of Explosives-Contaminated Piping and Debris. Revision 2. Prepared by Roy F. Weston, Inc. January 1996.

- Octahydro-1,3,5,7 tetrinitro-1,3,5,7-tetrazocine (HMX)
- Hexahydro-1,3,5-trinitro-s-triazine (RDX)
- 1,3,5-Trinitrobenzene (1,3,5-TNB)
- 1,3-Dinitrobenzene (1,3-DNB)
- Nitrobenzene (NB)
- 2,4,6-Trinitrophenylmethylnitramine (Tetryl)
- 2,4,6-Trinitrotoluene (2,4,6-TNT)
- 2,6-Dinitrotoluene (2,6-DNT)
- 2,4-Dinitrotoluene (2,4-DNT)

Following treatment, wipe samples were taken from all spiked test plates. Clay and block test plates were then ground into a powder and analyzed for explosives residuals. The contaminated debris from the ALAAP remediation was wipe sampled before treatment to verify contamination levels. A combination of wipe and ground samples were taken after treatment to verify that no explosives residuals remained on the contaminated debris or test plates

To support validation testing, a rigorous emissions testing program was conducted during the first three validation test runs to support future permitting efforts of the hot-gas process by USAEC and to determine the system and afterburner destruction and removal efficiencies (DRE's). Hot-gas stack emissions were sampled for:

- Carbon Monoxide
- Carbon Dioxide
- Oxygen
- Total Hydrocarbons (stack and interconnecting duct)
- Nitrous Oxides (stack and interconnecting duct)
- Sulfur Dioxide
- Particulate
- Explosives
- Volatile and Semi-volatile Organics
- Metals
- Hexavalent Chromium
- Hydrochloric Acid and Chlorine Gas
- Dioxins and Furans

The stack team also took an explosives sample at the interconnecting duct between the furnace exit and afterburner inlet to support DRE calculations.

Stack emissions were monitored during all test runs by a Continuous Emissions Monitoring (CEM) system for the following constituents: carbon dioxide (CO₂), carbon monoxide (CO), total hydrocarbons (THC), oxides of nitrogen (NO_x), sulfur dioxide (SO₂), and oxygen (O₂). To gather

information regarding the furnace off-gas flow during decontamination activities, a THC and NO_x sample probe were placed in the interconnecting duct between the furnace exit and afterburner entrance.

Spiking, Furnace Loading and Operations

For each of the 15 test loads the furnace was charged with a combination of clean steel pipe, clean clay pipe, and clean cinder block. For test runs #4 through #15, contaminated debris from the ALAAP remediation was also loaded into the furnace. The contaminated debris had been pressure washed to meet 3X criteria and consisted of concrete chunks, rocks, old valves, and pieces of metal and clay piping. Because of permitting limitations, no more than 800 pounds of pre-contaminated material could be placed in any batch run. Because of equipment design limits, no more than 3,000 pounds total was loaded into the furnace for per batch run.

To support DRE calculations and evaluate the effectiveness of the hot-gas process, each test load contained 3 steel test plates, 3 clay test plates, and 3 concrete block test samples. These test plates and samples where spiked with either TNT, RDX, or Tetral and placed throughout the test load within the furnace. Five furnace wall plates: 2 test plates on each side wall and 1 on the furnace door, were also spiked during each test run. Each of the 5 furnace plates were spiked with the same spike mixture within a test run, but alternated between TNT, Tetral, and RDX between test runs. For instance, furnace test plates were spiked with: TNT for Test #1, RDX for Test #2, Tetral for Test #3, TNT for Test #4, etc. Spike mixtures were made by combining the pure explosive (TNT, RDX or Tetral) with enough acetone to form a paste-like consistency. Each test plate or sample was spiked with approximately 15-20 grams of a single spike mixture. Although TNT, RDX and Tetral test plates were treated in each test run, spike mixtures were not mixed together on the same test specimen.

Once charged, the furnace door is secured and the decontamination process can be started. From start to finish a complete hot-gas test run consists of the following tasks:

- Spiking test plates and samples, if applicable
- Loading the furnace
- Afterburner start-up time necessary to reach 1,800°F.
- Furnace ramp-up time
- Material soak time, if used
- Burner shutdown
- Material cool-down time
- Post test sampling, if applicable.

Total test time will vary depending on the selected ramp-up rate to treatment temperature and soak times. For a series of 19 batch runs (15 validation tests plus 4 confirmation runs) conducted by WESTON, total treatment times varied from 13 hours for Test #1 to approximately 4 hours for Tests #16A - #16C which were conducted with no soak times. Since both the furnace and afterburner are lined with a ceramic-fiber insulation heat-up rates of 30-60 minutes were possible. Ramp-up rates to treatment temperature, treatment temperatures, and soak times at treatment temperature were varied. Ramp-up times varied from 50°F/hr during the first three validation test runs to 300°F/hr for some of the final test runs. As illustrated in Table 1, treatment temperatures varied between 300°F and 600°F and soak times varied between 0-12 hours. The conclusions drawn from these variations in ramp-up

times, treatment temperatures and soak times will be discussed in more detail in "Discussion of Results" section of this paper.

DISCUSSION OF RESULTS

After each test run test plates were sampled and analyzed for residual explosives-concentrations. In analyzing the results, WESTON established three levels of acceptance criteria to determine the effectiveness of the HGD process.

Acceptance Level 1: To pass this acceptance criteria post-treatment analysis must indicate 99.9999% or better removal efficiency of the spike explosives. Residual levels of explosives or explosives-breakdown compounds would not necessarily fail this criteria.

Acceptance Level 2: To pass this acceptance criteria post-treatment results must indicate the removal of all spike explosives compounds. The presence of TNT, RDX or Tetryl residuals would fail a test plate or sample. Removal efficiency was not considered.

NOTE: A sample which passed Level 1 criteria could fail this level due to trace levels of the spike explosives.

Acceptance Level 3: To pass this acceptance level the post-treatment sample must be completely free of explosives or explosives-breakdown compounds.

This was the toughest criteria to meet. Specimens which pass Level 1 and 2 criteria could fail this acceptance level due to trace levels of explosives-breakdown compounds, such as 1,3 DNT, regardless of detection level.

Discussion of Level 3 Results:

Table 2 provides a test matrix indicating the results of the validation tests using the most stringent acceptance level, Level 3. The dark, shaded blocks indicate failure or the presence of explosives or explosives-breakdown compounds regardless of detection level. Depending on the test conditions detection limits were as high as 18,000 μ g and low as 0.5 μ g.

Using the level 3 acceptance criteria, the data included on Table 2 indicates that explosives-contaminated materials can be decontaminated (no traces of explosives or explosives-breakdown compounds) at treatment temperatures of 600°F and 1-hour soak (Test #7, #14, #15). In tests #7, #14, #15, all traces of explosives were successfully decontaminated from the spiked test plates and samples. Tests #7 and #14 also successfully decontaminated the pre-contaminated debris. Test #15, failed due to traces of 1,3,5-TNB and 2,4,6-TNT (0.5 μ g and 0.7g, respectively). Although this level of contaminants is clearly non-reactive, they may not be low enough to pass a local treatment criteria.

In contrast, tests which were conducted at 600°F and no soak time (#9, #16A, #16B, and #16C) were only partially successful. Although test #9 failed contaminated debris for trace levels of 1,3,5-TNB and 2,4,6-

Table 2: LEVEL 3 ACCEPTANCE CRITERIA

No Soak	300°F				400°F				500°F				550°F				600°F				600°F				600°F					
	TNS	TNC	TNB	FP-Te																										
1 hr Soak	TNS	TNC	TNB	FP-Te																										
	R-S	R-C	R-B	D-Te	R-S	R-C	R-B	Dup	R-S	R-C	R-B	D	R-S	R-C	R-B	D	R-S	R-C	R-B	D	R-S	R-C	R-B	D-Te	R-S	R-C	R-B	D-Te		
	Te-S	Te-C	Te-B	Cont																										
2 hr Soak																														
	TNS	TNC	TNB	FP-Te																										
	R-S	R-C	R-B	Dup	R-S	R-C	R-B	D	R-S	R-C	R-B	D-Te	R-S	R-C	R-B	D-Te														
	Te-S	Te-C	Te-B	Cont																										
4 hr Soak																														
	TNS	TNC	TNB	FP-Te																										
	R-S	R-C	R-B	D-Te	R-S	R-C	R-B	D	R-S	R-C	R-B	D-Te	R-S	R-C	R-B	D-Te														
	Te-S	Te-C	Te-B	Cont																										
6 hr Soak																														
	TNS	TNC	TNB	FP-Te																										
	R-S	R-C	R-B	D-Te	R-S	R-C	R-B	D	R-S	R-C	R-B	D-Te	R-S	R-C	R-B	D-Te														
	Te-S	Te-C	Te-B	Cont																										
12 hr Soak																														
	TNS	TNC	TNB	FP-Te																										
	R-S	R-C	R-B	D	R-S	R-C	R-B	D-Te	R-S	R-C	R-B	D-Te																		
	Te-S	Te-C	Te-B	Cont																										

Key:**TNC** - Failed**TNC** - Passed

50°F/hr Ramp: Tests 1, 2 & 3

75°F/hr Ramp: Tests 4, 5, & 6

100°F/hr Ramp: Tests 7, 8 & 9

150°F/hr Ramp: Tests 10 & 11

200°F/hr Ramp: Tests 12 & 13

300°F/hr Ramp: Tests 14 & 15

B- Block

TN - TNT

FP - Furnace Plates

D - Duplicated Test Plate and Analysis

Cont - Contaminated Debris After Treatment

C- Clay

Te-Tetyl

S- Steel

R - RDX

TNT ($1.4\mu\text{g}$ and $2.2\mu\text{g}$, respectively), Tests #16A and #16B failed to successfully decontaminate concrete blocks which had been spiked with TNT or Tetryl. Test #16A treated only TNT-contaminated samples. Test #16B treated on Tetryl-contaminated samples. Post-treatment samples of TNT-spiked blocks from Test #16A contained levels as high as $7,962\mu\text{g}$ 2,4,6-TNT and $10,000\mu\text{g}$ of 2,4-DNT. Post-treatment samples of Tetryl-spiked blocks taken after Test#16B contained levels of 1,3,5-TNB from $0.6\text{--}191\mu\text{g}$. In Tests #16B and #16C (RDX only), some of the furnace test plates, 5 located around the inside perimeter of the furnace walls and door failed to meet treatment criteria.

The failures clearly point to the importance of treatment temperature in decontaminating explosives-contaminated materials. In each test load spiked steel pipe, spiked clay plates and spiked clay blocks were treated. Pre-contaminated debris (metal valving and pipes, chunks of concrete) from the remediation effort were placed with like items in the furnace. For each test run 5 load thermocouples were placed throughout the load to track material temperatures during the test. The average of the five thermocouples was used to define the treatment temperature. When the average thermocouple value, as tracked by the datalogger, was equal to 600°F , the soak time was begun. In the case of a zero soak time, the test run was completed. Figure 2, 3 and 4 provides a comparison of steel, clay and block temperatures respectively at the end of ramp, and soak times for Tests #7, #9, #14, #15, #16A and #16B. Test #7 and #9 were performed with a slow heat ramp-up rate of 100°F per hour. Test #14 and #15 were controlled at a faster heat -up ramp-up rate 300°F . Test 16A and 16B were heat-up as fast as possible within the heat limit of the HGD system. Tests #9, #16A and #16B were conducted at 600°F and zero soak time. Tests #7, #14 and #15 were conducted at 600°F and 1-hour soak time.

For steel, Figure 2 shows that at a temperature of 565°F , which can be reached as little as 1 hours and as long as 5 hours and 15 minutes, can effectively treat concrete surface contamination. For clay, Figure 3 shows that at a average temperature of 571°F , which can be reached as little as 1 hour 5 minutes and as long as 4 hours 35 minutes, can effectively treat explosives-contaminated clay material. For concrete, Figure 4 show that the material must reach 513°F between 2 hours and 5 hours. Test #16A and 16B failed because the surface temperature never reached above the 513°F before the tests was stopped. However, if the test were continued at the same heat-up rate, the material could have reached the treatment temperature in less than 1 hour and 34 minutes.

From the graphs presented in Figure 2, 3, and 4 one fact becomes clear: material temperatures between the ranges of $513\text{--}565^\circ\text{F}$ is required to successfully decontaminate explosives-contaminated material. Materials which do not reach this temperature range (i.e., block samples from Tests#16A and #16B) are not completely decontaminated. Soak times and ramp-up times are of little importance as long as material temperatures reach the minimum required treatment temperature. However, to reduced the total processing time, a faster heat-up rate is preferred. The HGD process can heat up concrete up to the treatment temperature range in less than 2 hours. The graph also indicates the advantages in processing loads of similar materials so that the temperature differential problems (i.e., between steel and block) could be avoided.

Throughout testing, regardless of test conditions, TNT proved the most difficult explosives compound to decontaminate and RDX the easiest compound. Test #2 was conducted at 300°F in order to achieve define a temperature which **did not** successfully treat RDX. Non-porous materials (steel) were easier to decontaminate than more porous materials such as clay or concrete, however once materials treatment temperatures of at least 513°F decontamination was achieved.

Figure 2: STEEL MATERIAL TEMPERATURE

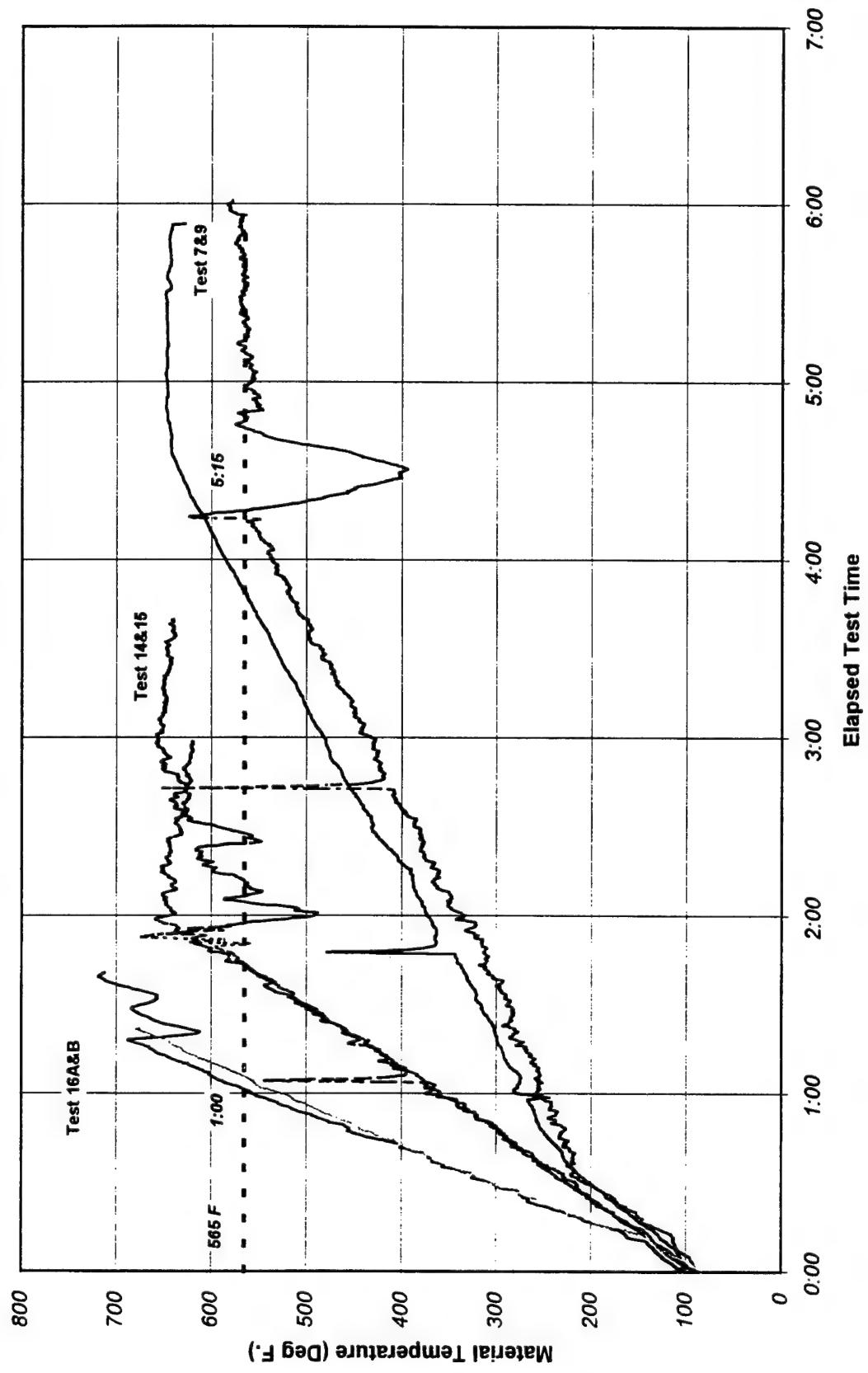


Figure 3: CLAY MATERIAL TEMPERATURE

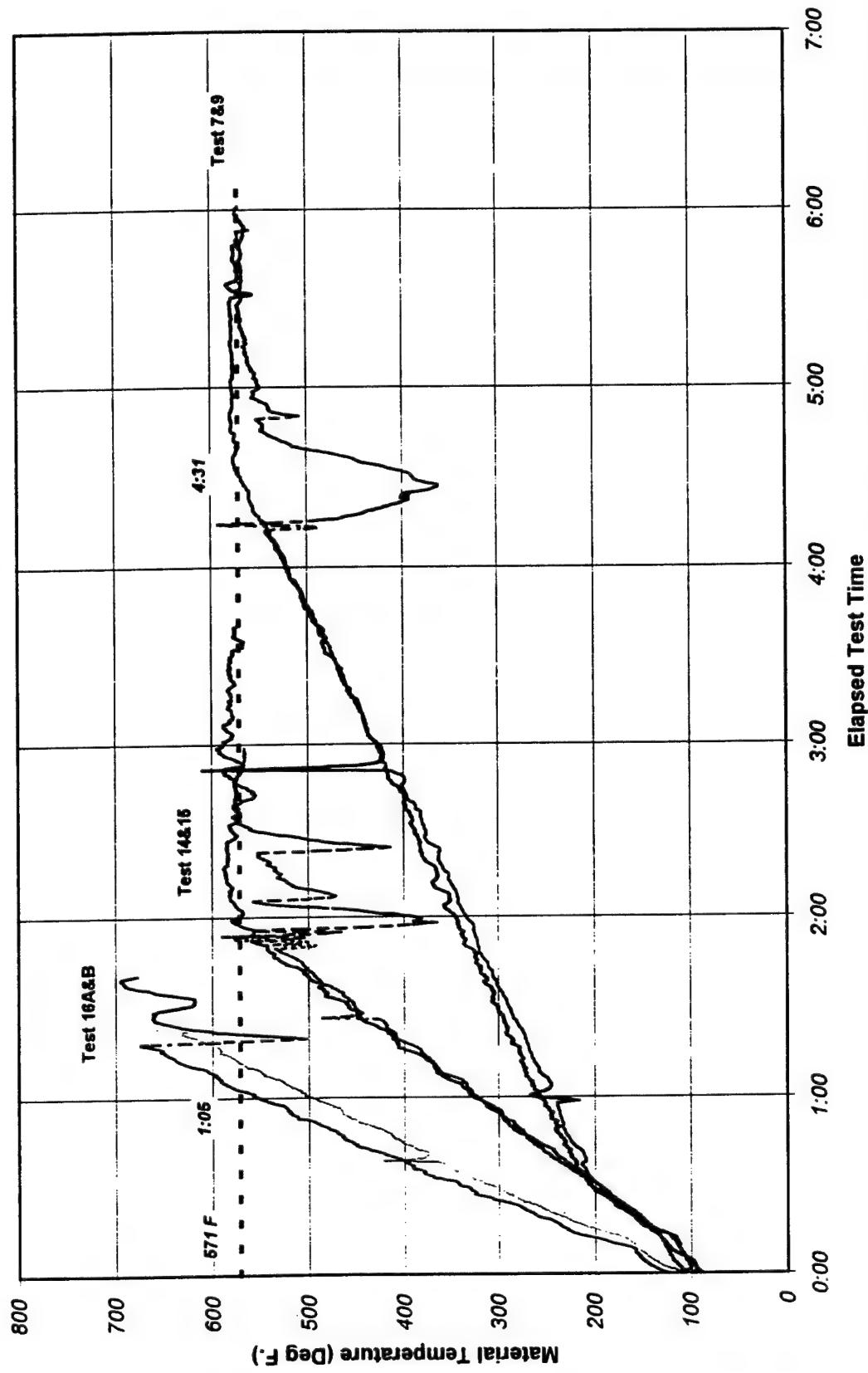
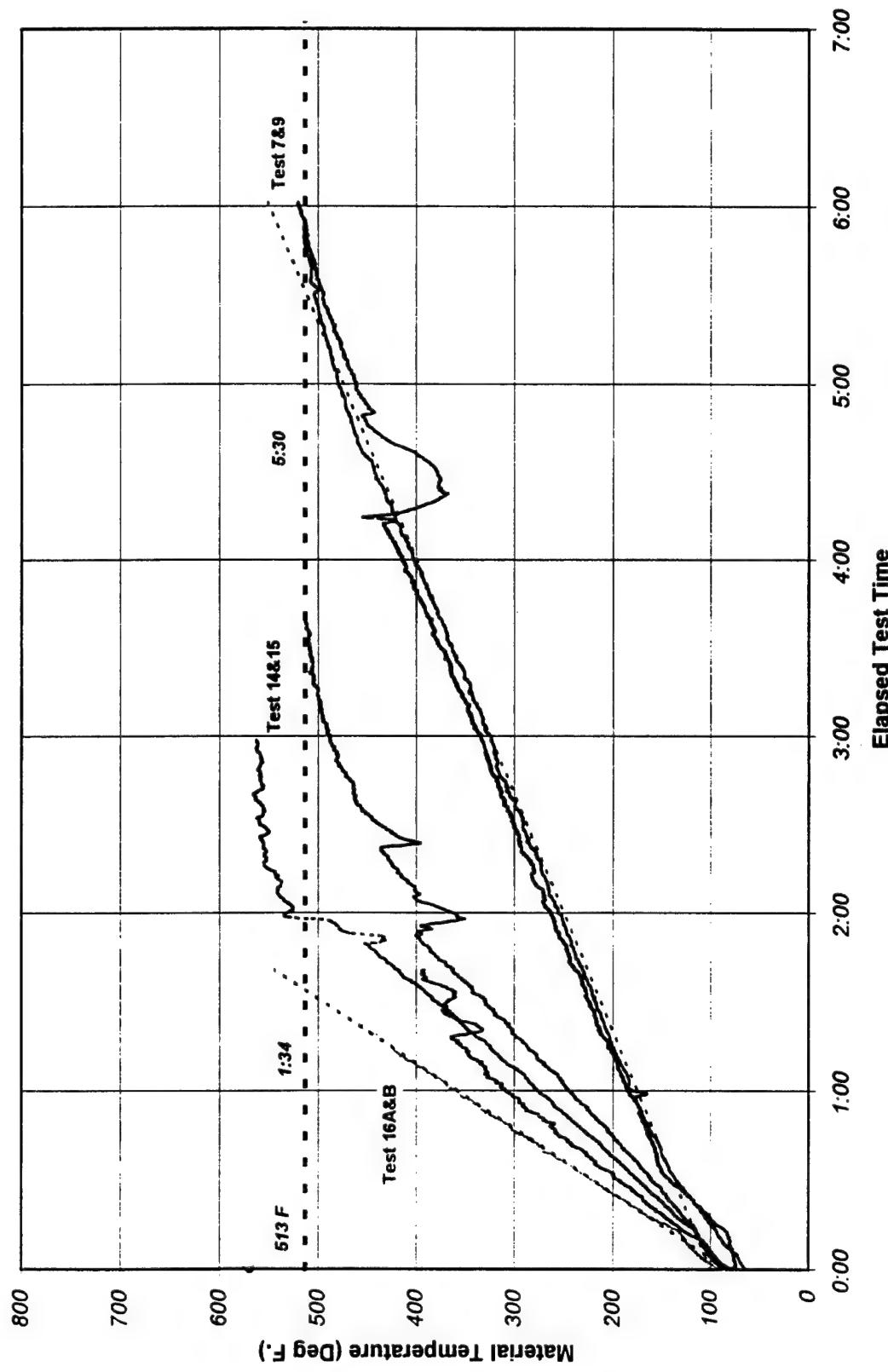


Figure 4: CONCRETE MATERIAL TEMPERATURE



A review of post-treatment sampling results indicates that many of the residual contamination levels are low; but are they low enough to pass standard accepted treatment criteria for explosives? In order to provide a comparison of the residual contamination levels found to an accepted treatment criteria, WESTON converted the residual levels of contaminants (μg) found on the post-treatment wipe and ground samples concentration ($\mu\text{g/g}$ for ground samples and $\mu\text{g/sq. in}$ for wipe samples). The resultant concentrations were graphed against pre-treatment concentration of spike explosives and compared against a 99.99% removal requirement. In the case of the ground samples the final concentration was also compared against a 1 ppm treatment criteria for explosives which WESTON is currently required by ADEM to meet prior to backfilling explosives-contaminated soils which have been incinerated. Figure 5 illustrates that all wipe samples, except for those taken following test (12 which was conducted at 300°F) were able to successfully pass the 99.99% removal criteria. Figure 6 indicates that all but one of the ground samples which passed the 99.99% removal criteria was able to pass the 2ppm backfill criteria. Those ground samples which did not meet the 99.99% removal criteria had not reached temperatures sufficiently hot enough to completely decontaminate the spike explosives.

Discussion of Level 2 Results:

Table 3 provides a test matrix indicating the results of validation tests meeting the acceptance criteria defined by Level 2. Dark, shaded blocks on Table 3 indicate post-treatment samples which still indicate some level of the original spike explosive. Failures noted on this table may have passed the 99.99% removal criteria, but still contain traces of the original spike explosives. Contaminated debris from the ALAAP remediation area were not considered in this acceptance level, because initial contamination levels were unknown.

Using Level 2 acceptance criteria, the data included on Table 3 indicates that the spike explosives were successfully decontaminated (no trace of the original spike explosives or breakdown compounds) at treatment temperatures of 600°F (Tests #5, #6, #7, #9, #14, #15, #16B, and #16C) regardless of soak time. Test #16A failed to meet level 2 criteria due to the inability to treat concrete block spiked with TNT. Sample blocks were spiked with quantities between 9.4 - 11.6 grams of TNT. Although the removal efficiencies for these samples were in the 99.92% range, the residual TNT levels after treatment were between 6,302 - 10,000 μg .

Because the treatment temperature was based on an average of 5 material thermocouples distributed throughout the load, it's suspected that the spiked test block did not reach a temperature which was high enough to completely vaporize the TNT on the test block. The system data logger indicated the highest surface temperature reached by the concrete blocks contained in the furnace load to be 394°F whereas the metal pipe in the load reached a treatment temperature as between 565-710°F.

Table 3 also indicates that spike explosives were successfully decontaminated (no trace of the original spike explosives or breakdown compounds) at treatment temperatures of 500°F (Tests #1, #3, #4, and #8) provided the soak time was greater than or equal to 2-hours. Test #13, which was conducted at 500°F and a 1-hour soak, failed the level 2 criteria because of a 66 μg hit of TNT found in the TNT ash residual left behind on a spiked furnace test plate located in the rear of the furnace. As noted earlier, TNT was the most difficult explosive to treat, but at treatment temperatures below 600°F TNT usually left an ash residual behind. The ash residual had a shiny, glass-like appearance. It was very light in weight and in most cases formed a "soufflé" on the test plates. In all cases the residual was sampled, by grinding the ash and then sampling the ground ash in accordance with Method 8330.

Figure 5: POST TREATMENT EXPLOSIVES RESIDUAL ANALYSIS (WIPE SAMPLES)

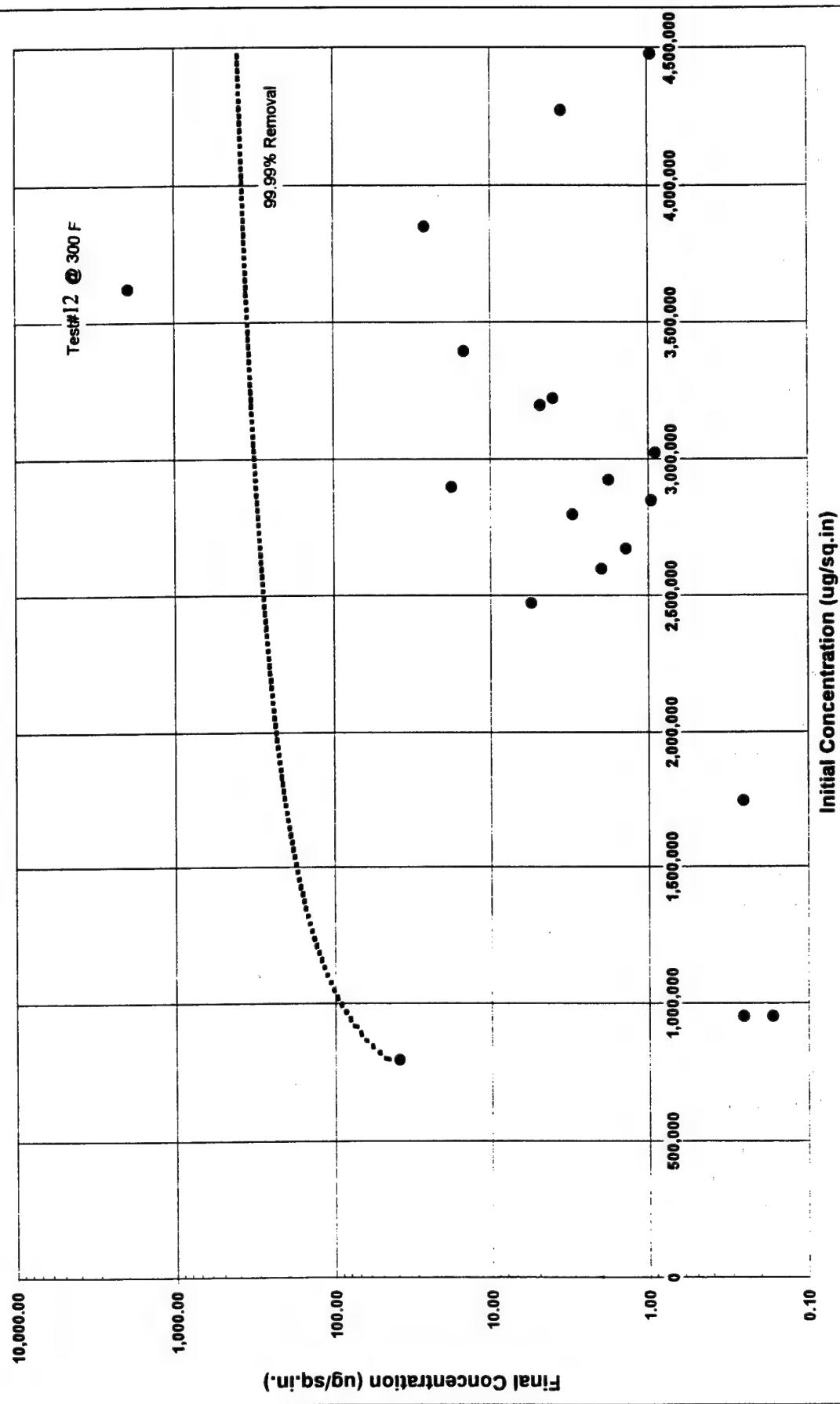


Figure 6: POST TREATMENT EXPLOSIVES RESIDUAL ANALYSIS (SOLID SAMPLES)

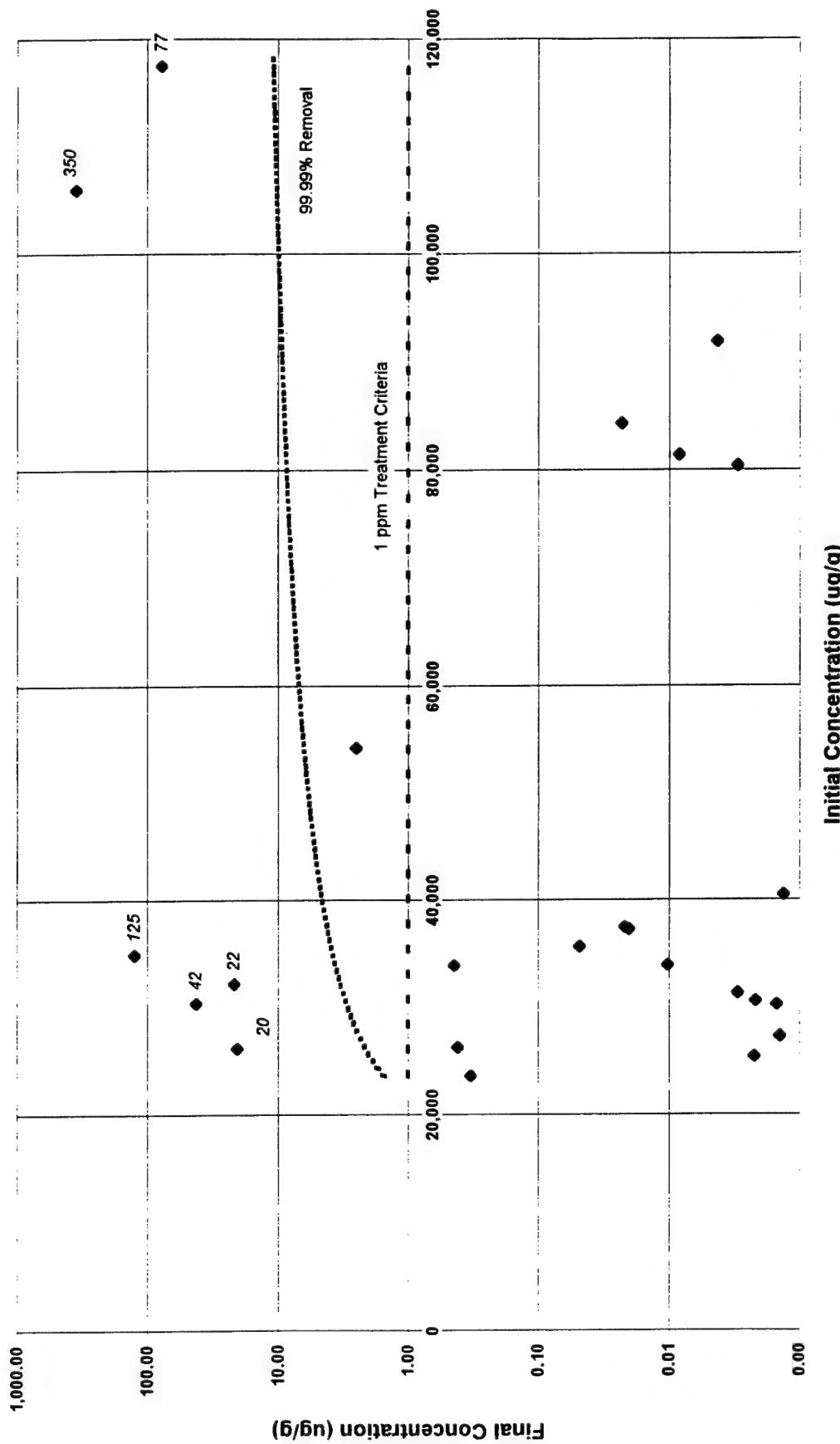


Table 3: LEVEL 2 ACCEPTANCE CRITERIA

Soak	300°F			400°F			500°F			550°F			600°F			600°F			600°F				
	Test #9: 6hr 16 min			Test #10: 4 hr 46 min			Test #11: 2 hr 41 min			Test #12: 3 hr 14 min			Test #13: 3 hr 14 min			Test #14: 3 hr 20 min			Test #15: 3 hr 3 min				
1 hr Soak	TN-S	TN-C	TN-B	FP-Te	TN-S	TN-C	TN-B	FP-R	TN-S	TN-C	TN-B	FP-TN	TN-S	TN-C	TN-B	FP-TN	TN-S	TN-C	TN-B	FP-TN	TN-S	TN-C	TN-B
R-S	R-C	R-B	D-Te	R-S	R-C	R-B	D-Te	R-S	R-C	R-B	D-Te	R-S	R-C	R-B	D-Te	R-S	R-C	R-B	D-Te	R-S	R-C	R-B	
Te-S	Te-C	Te-B		Te-S	Te-C	Te-B		Te-S	Te-C	Te-B		Te-S	Te-C	Te-B		Te-S	Te-C	Te-B		Te-S	Te-C	Te-B	
2 hr Soak																							
4 hr Soak																							
6 hr Soak																							
12 hr Soak																							

Keys:

TN-C	Passed
TN-C	Failed

50°F/hr Ramp: Tests 1, 2 & 3
75°F/hr Ramp: Tests 4, 5, & 6
100°F/hr Ramp: Tests 7, 8, & 9
150°F/hr Ramp: Tests 10 & 11
200°F/hr Ramp: Tests 12 & 13
300°F/hr Ramp: Tests 14 & 15

Discussion of Level 1 Results

Table 4 provides a test matrix indicating the results of the validation tests using Level 1 acceptance criteria. Level 1 was the easiest acceptance criteria to meet. Dark, shaded squares indicate failures or post-treatment samples which contained explosives residuals levels in excess of 99.9999% removal. Contaminated debris from the ALAAP remediation area were not considered for this acceptance level, because initial contamination levels were unknown.

In general Level 1 results mirror the test data presented in Table 3: spike explosives were successfully decontaminated ($> 99.9999\%$ removal) at treatment temperatures between 550°F and 600°F (Tests #5, #6, #7, #10, #14, and #15,) and a soak time of at least 1 hour. Although tests conducted at 500°F (Tests #13 and #8) pass the 99.9999% removal criteria, and successfully decontaminated the spike explosives, some explosives- breakdown compounds still remain as indicated on Table 2 which evaluated the same data to Level 3 criteria.

HGD Emissions Results

Stack monitoring was conducted to provide an indicator of total system performance, and to provide "real" data to support future permitting efforts. Sampling trains were located at the interconnecting duct between the furnace exit and afterburner entrance, and at the stack discharge to determine the DRE of the hot-gas decontamination process. Sampling was conducted for Test #1, #2 and #3. Since the amount of emissions data generated during the validation tests is immense, a tabulation of the testing results will be presented. Each of the tables presenting stack data indicate "hits" only.

Explosives emissions at the system stack were sampled using EPA Method 0010. The results, presented in Table 5, indicate no detectable explosives-contamination were observed in the stack emission of the hot-gas system. Explosives samples taken at the interconnection duct indicate that explosives-contamination in the furnace is vaporized, and drawn through the duct prior to destruction in the system afterburner. During Test #1 a mid-soak explosives sample was also taken. This sample was taken between hours 4.5 and 7, and corresponded to the middle of the 12-hour soak period associated with Test #1. Based on previous tests, it was suspected that the majority of decontamination occurs during the heat-up and early stages of the soak period. The purpose of mid-soak sample was to verify that suspicion. As indicated by Table 6, no explosives were detected in the mid-soak sample, thereby confirming that little or no decontamination occurs 4-hours into the soak period. The overall destruction and removal efficiencies for the overall hot-gas system and afterburner system are indicated on Table 7.

Particulate, Chlorine gas (Cl_2), and hydrochloric acid (HCl) emissions were sampled using EPA Method 0050. The filterable particulate analysis was performed using Method 5; Method 9057 (ion chromatography) was used to determine HCl and Cl_2 levels. The results are presented in Table 6. The regulatory criteria for particulate emissions is < 0.08 grains per dry standard cubic feet (gr./dscf) corrected to 7% O_2 . Particulate results from the validation tests #1-#3 were well below the regulatory criteria and ranged from 0.000222 to 0.000656 gr./dscf @ 7% O_2 . HCl emissions for Tests #1, #2, and #3 were 0.00177, 0.0015 and 0.0014 lbs/hr , respectively which are well below the regulatory limit of 4 lbs/hr. Emissions limits for chlorine gas do not exist unless defined by a tier analysis, however chlorine gas emissions for all Tests #1-#3 were 2.06×10^{-4} , 0.00105 and 0.00108 lbs/hr. Metals stack emissions were sampled for the following metals in accordance with draft EPA Method 29: antimony, arsenic, barium, beryllium, cadmium, chromium, lead, mercury, nickel, selenium, silver, thallium and hexavalent chromium. Hexavalent chromium was sampled in accordance with EPA CR⁺⁶ Method..

Table 4: LEVEL 1 ACCEPTANCE CRITERIA

	300°F			400°F			500°F			550°F			600°F			600°F			600°F				
	Test #11: 2 hr 41 min			Test #12: 3 hr 8 min			Test #13: 3 hr 14 min			Test #14: 4 hr 46 min			Test #15: 6 hr 15 min			Test #16: 7 hr 63 min			Test #17: 7 hr 20 min			Test #18: 3 hr 3 min	
No Soak	TN-S	TN-C	TN-B	FP-Te	TN-S	TN-C	TN-B	FP-Te	TN-S	TN-C	TN-B	FP-Te	TN-S	TN-C	TN-B	FP-Te	TN-S	TN-C	TN-B	FP-Te	TN-S	TN-C	TN-B
1 hr Soak	R-S	R-C	R-B	D	R-S	R-C	R-B	D	R-S	R-C	R-B	D	R-S	R-C	R-B	D	R-S	R-C	R-B	D	R-S	R-C	R-B
	Te-S	Te-C	Te-B		Te-S	Te-C	Te-B		Te-S	Te-C	Te-B		Te-S	Te-C	Te-B		Te-S	Te-C	Te-B		Te-S	Te-C	Te-B
2 hr Soak																							
4 hr Soak																							
6 hr Soak																							
12 hr Soak																							

Keys:

TN-S | Failed

TN-C | Passed

50°F/hr Ramp: Tests 1, 2 & 3
 75°F/hr Ramp: Tests 4, 5, & 6
 100°F/hr Ramp: Tests 7, 8, & 9
 150°F/hr Ramp: Tests 10 & 11
 200°F/hr Ramp: Tests 12 & 13
 300°F/hr Ramp: Tests 14 & 15

Table 5: SUMMARY OF EXPLOSIVE COMPOUNDS

Explosives Emissions: ppb/v	Date: 31-Jan-96 Time: 1832-0122	At Furnace Discharge			At Afterburner Discharge		
		Test Run #1 Mid-Soak 1-Feb-96 0644-1005	Test Run #2 2-Feb-96 1405-2100	Test Run #3 4-Feb-96 1406-2106	Test Run #1 Mid-Soak 1-Feb-96 —	Test Run #1 2-Feb-96 1406-2031	Test Run #3 4-Feb-96 1409-2036
HMX	ND	ND	ND	ND	ND	—	ND
RDX	24.23	0.06	54.30	23.20	ND	—	ND
Trinitrobenzene (1,3,5-TNB)	11.49	0.30	11.38	9.98	ND	—	ND
Dinitrobenzene (1,3-DNB)	0.24	ND	0.23	0.60	ND	—	ND
Nitrobenzene (NB)	ND	ND	ND	ND	ND	—	ND
Tetryl	3.16	ND	2.99	1.90	ND	—	ND
2,4,6-Trinitrotoluene (TNT)	707.18	5.33	192.26	193.24	ND	—	ND
2,6-Dinitrotoluene (2,6-DNT)	ND	ND	0.48	ND	ND	—	ND
2,4-Dinitrotoluene (2,4-DNT)	1.20	ND	ND	ND	ND	—	ND

ND - Analyte detected at less than the detection limit value

Midsoak - This sample was taken between hours 4-7 of the 12 hour soak period of Test Run #1

Table 6: OVERALL HOT GAS SYSTEM REMOVAL EFFICIENCY

Explosive Removal Efficiency (%)	Overall Hot Gas System Removal Efficiency ⁽¹⁾			Afterburner Removal Efficiency ⁽²⁾		
	Test Run #1 31 Jan 96	Test Run #2 2 Feb 96	Test Run #3 4 Feb 96	Test Run 1 31 Jan 96	Test Run 2 2 Feb 96	Test Run 3 4 Feb 96
2,4,6 - Trinitrotoluene (TNT)	>99.97	>99.95	>99.94	>99.97	>99.86	>99.86
Tetryl	>99.79	>99.92	>99.94	>84.91	>79.09	>67.15
RDX	>99.88	>99.97	>99.91	>98.30	>99.00	>97.68

⁽¹⁾ Based on total explosives introduced to furnace converted to lb/hr (using total test times) and afterburner discharge mass rate determination for each explosive.

⁽²⁾ Afterburner removal efficiency based on the following: % RE =
$$\frac{\text{AFT IN} - \text{AFT OUT}}{\text{AFT IN}} \times 100$$

NOTES: All removal efficiencies reported as greater than since no explosives were measured above the method detection limit at the afterburner discharge.

lbs/hr, respectively for Tests #1-#3. Mercury emissions levels were less than 1.37×10^{-7} lbs/hr. Hexavalent chromium emissions were, as expected, negligible (refer to Table 5). The metals and hexavalent chromium results are provided in Table 7. Allowable emissions limits for these metals are normally established using a tier analysis and modeling, however, total metals emissions, not including hexavalent chromium and mercury, were calculated to be $< 9.74 \times 10^{-5}$ lbs/hr, $< 6.04 \times 10^{-5}$ lbs/hr, and 3.65×10^{-5} lbs/hr, respectively for tests #1 - #3. Total carcinogenic metals (Arsenic, Beryllium, Cadmium, and Chromium) emissions were calculated to be $< 5.19 \times 10^{-5}$ lbs/hr, $< 5.09 \times 10^{-5}$ lbs/hr, and 3.95×10^{-5}

Volatile and semi-volatile compounds found in the stack emissions are presented in Tables 8. These tables identify both products of incomplete combustion and breakdown components as a result of treating explosives. High levels of acetone (0.145, 0.0798, and 0.0399 ppm/volume) were found in the volatile organics analysis and occur as a result of using acetone to make the explosives-spike mixtures. Semi-volatile samples were analyzed for TCL semi-volatile target compounds. Only non-target compounds were identified. The -thalate compounds identified are due to lab solvents used in the sample extraction process.

Dioxin and furan data is reported in Table 9. The total detected 2,3,7,8-TCDD Equivalents for tests #1, #2, and #3 were 0.0395, 0.0221, and 0.0309 ng/dscm which are well below the 30 total ng/dscm suggested by the existing guidelines.

The results from the stack continuous emissions monitoring (CEM) system indicate that total hydrocarbons (THC), sulfur dioxide (SO₂), Nitrous Oxides (NO_x), Carbon monoxide (CO), and Carbon Dioxide (CO₂) were significantly below the allowable limits usually associated with permitting. Since testing was conducted under the rules of a treatability study, meeting a permitted limit was not required, however, in actual applications it would be expected that standard accepted regulatory limits defining CO, CO₂, THC and NO_x would apply.

Of particular interest during all the validation tests was the NO_x data. NO_x was measured at both the interconnecting duct and the stack. During ramp-up periods for each test run, the CEM data indicated increased NO_x activity well above the baseline level of non-detected, until the average load temperature (as measured by 5 thermocouples placed throughout the load) reached approximately 400°F. This seemed to be an indication that the bulk of decontamination activity was complete. Shortly after reaching 400°F, the NO_x analyzers would return to baseline non-detected levels.

CONCLUSIONS

The Hot Gas Decontamination (HGD) Demonstration Program at ALAAP demonstrated the solidness of the equipment design, and efficacy, safety, and economics of the HGD process to remove and destroy explosives residues such as TNT, RDX, and Tetryl from metal, clay, and concrete piping and debris.

Using the most stringent acceptance criteria, an average load temperature of 600°F with a 1-hour soak time is sufficient to decontaminate a 3.000 LB load of piping and debris which has been contaminated with quantities of TNT, RDX and Tetryl which total no more than 1 LB explosives.

Test results indicated that TNT was the hardest explosive to completely decontaminate (600°F, 1 hour soak), while RDX was the easiest (400°F, soak). In addition to the recommended optimum treatment conditions, test results also indicate that the HGD process was able to effectively decontaminate

Table 7: METALS, HCL, CL₂ AND PARTICULATE EMISSION RESULTS

Metals Emissions Rate lbs/hr	Date: 31-Jan-96 Time: 1834-0103	Test Run #1 2-Feb-96 1406-2011	Test Run #2 4-Feb-96 1415-2026
Antimony	4.11E-06	9.54E-07	<1.11E-05
Arsenic	<7.50E-06	<7.38E-06	<7.46E-06
Barium	2.16E-05	2.78E-07	2.16E-07
Beryllium	1.96E-08	<2.40E-08	<2.45E-08
Cadmium	1.57E-06	7.57E-07	<6.87E-07
Chromium	4.28E-05	4.27E-05	3.13E-05
Lead	1.70E-05	3.55E-06	2.45E-06
Mercury	1.37E-07	2.35E-07	2.95E-08
Nickel	1.03E-05	1.22E-05	2.55E-06
Selenium	<8.68E-06	<8.53E-06	<8.64E-06
Silver	<2.20E-06	<2.16E-06	<2.20E-06
Thallium	<7.65E-06	<7.48E-06	<7.66E-06
Hexavalent Chromium **	5.10E-05	5.29E-05	3.85E-05
HCL, ppm/v	0.31	0.27	0.27
Cl₂, ppm/v	0.019	0.098	0.109
Particulate , gr/dscf @ 7% O₂	4.52E-04	2.22E-04	6.56E-04

< Indicates the analyte was detected at values less than the detection limit indicated

** The hexavalent chromium values reported may not be truly representative.

The hexavalent chromium values exceed the total chromium values obtained using the multi-metals test train.

The hexavalent chromium test train has not been validated by EPA for use on sources > 300°F

Table 8: VOLATILE AND SEMI-VOLATILE ORGANIC COMPOUNDS

Average** VOST Emissions, ppm/v	Date:	Test Run #1	Test Run #2	Test Run #3	Average VOST Emissions
	Time:	31-Jan-96 1846-2322	2-Feb-96 1419-2005	4-Feb-96 1418-1950	
Chloromethane (Methyl Chloride)		6.78E-02	1.59E-02	3.03E-02	3.80E-02
Bromomethane (Methyl Bromide)		3.18E-03	1.22E-03	2.04E-03	2.15E-03
Methylene Chloride		9.84E-04	9.55E-04	1.19E-03	1.04E-03
Acetone		1.45E-01	7.98E-02	3.99E-02	8.82E-02
Carbon Disulfide		<	3.18E-04	2.10E-04	1.76E-04
Chloroform		1.82E-04	1.80E-04	1.14E-04	1.59E-04
Benzene		9.70E-04	2.72E-04	3.78E-04	5.40E-04
Toluene		4.72E-04	1.07E-04	1.22E-04	2.34E-04
Styrene		1.14E-04	4.37E-04	4.28E-04	3.26E-04
Xylenes (total)		2.76E-04	2.85E-04	2.01E-04	2.54E-04

Semivolatile Emissions: ppb/v	Test Run #1	Test Run #2	Test Run #3
Diethylphthalate	0.168 J	0.73 J	ND
Pentachlorophenol	0.05 J	0.25 J	ND
Di-n-butylphthalate	0.08 J	ND	ND
Benzo(a)anthracene	ND	0.06 J	ND
Chrysene	ND	0.04 J	ND
bis(2-Ethylhexyl)phthalate	0.28 JB	0.13 JB	0.15 JB
Di-n-octylphthalate	ND	0.02 J	ND

< Indicates value less than detection limits

** Detection Limit Values are included in the overall average

J = Detected in samples in quantities less than the detection limits

B = Detected in field blank in quantities greater than the samples, therefore the sample values are not blank corrected

Table 9: DIOXIN AND FURAN EMISSION RESULTS

Detected Toxicity Equivalency Emissions, ng/dscm	Date: 31-Jan-96 Time: 1834-0121	Test Run #1	Test Run #2	Test Run #3
	2-Feb-96 1405-2038	4-Feb-96 1410-2045		
2,3,7,8-TCDD	7.82E-03	4.09E-03	4.39E-03	
1,2,3,7,8-PeCDD	1.56E-02	7.17E-03	1.21E-02	
1,2,3,4,7,8-HxCDD	2.54E-03	1.23E-03	1.32E-03	
1,2,3,6,7,8-HxCDD	2.93E-03	1.02E-03	1.54E-03	
1,2,3,7,8,9-HxCDD	6.45E-03	2.25E-03	3.95E-03	
1,2,3,4,6,7,8-HpCDD	2.35E-03	6.96E-04	1.60E-03	
OCDD	6.06E-04	2.25E-04	4.39E-04	
2,3,7,8-TCDF	ND	2.05E-04	2.20E-04	
1,2,3,7,8-PeCDF	ND	1.02E-04	2.20E-04	
2,3,4,7,8-PeCDF	ND	3.07E-03	2.20E-03	
1,2,3,4,7,8-HxCDF	3.91E-04	8.19E-04	1.32E-03	
1,2,3,6,7,8-HxCDF	1.96E-04	4.09E-04	6.59E-04	
2,3,4,6,7,8-HxCDF	3.91E-04	6.14E-04	6.59E-04	
1,2,3,7,8,9-HxCDF	ND	ND	ND	
1,2,3,4,6,7,8-HpCDF	9.78E-05	1.64E-04	2.20E-04	
1,2,3,4,7,8,9-HpCDF	1.96E-05	2.05E-05	4.39E-05	
OCDF	1.56E-05	1.02E-05	1.10E-05	
Detected Total 2,3,7,8-TCDD Equivalents, ng/dscm	0.0395	0.0221	0.0309	

Calculated Total 2,3,7,8-TCDD equivalents based on detected values only

explosives-contaminated debris to microgram quantities while achieving at least 99.99 % destruction and removal efficiency at a full range of additional treatment temperatures and soak times.

For any group interested in using this process, we recommend a pilot run to verify the optimum treatment temperatures and times for your special loading conditions and contaminants. A pilot run will also allow the user to verify the presence or lack of breakdown compounds which could affect acceptance criteria.

In summary, based on WESTON's experience using the transportable hot-gas decontamination equipment at the ALAAP for the decontamination of explosives-contaminated piping and debris, a number of potential advantages as well as a few disadvantages were identified.

Assuming 5X decontamination is the goal, the hot-gas process has the following advantages over open burning/open detonation and/or using a flash furnace:

- Safer operation and reduced health risk to operators
- The ability to 5X decontaminate complicated machinery without destroying the structural integrity of the machinery
- The process can be designed to meet or exceed mandated air quality emissions
- Night or day operation, which is not generally affected by the weather conditions
 - Treated materials could be reused instead of scrapped or landfilled
- The hot-gas process is a proven and easily available technology
- The system is easy to operate and can be operated with as few as two persons
- Process equipment can be either permanent or transportable to suit operations needs

Assuming 5X decontamination, the hot-gas process has the following disadvantages when compared to open burning/open detonation and/or using a flash furnace:

- The initial cost of capital equipment and the ongoing cost associated with operating the equipment
- Materials should be decontaminated to meet 3X conditions prior to processing
- Further testing is required to verify the effectiveness of the hot-gas process on energetic
- The 5X definition (materials heated to at least 1,000°F for at least 15 minutes) needs to be revised to include the Hot-Gas process

The Internal Combustion Engine as a Low-Cost Soil Vapor Treatment Technology

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1.0 ABSTRACT

A low-cost and innovative soil vapor extraction (SVE) system using modified internal combustion engines (ICEs) to extract and destroy fuel hydrocarbons is successfully remediating a large JP-4 jet-fuel-contaminated site on Davis-Monthan Air Force Base (DMAFB), Arizona. Based on previous site investigations, soil contamination extended from near the ground surface to a depth of approximately 260 feet below ground surface (bgs). A maximum total fuel hydrocarbon concentration of 320,000 milligrams per kilogram (mg/kg) and a maximum soil gas hydrocarbon vapor concentration of 140,000 milligrams per liter (mg/L) were measured at the site. Prior to installing the full-scale SVE system using the ICE technology, bioventing and SVE with thermal oxidation were evaluated and determined not to be cost effective technologies for this site.

In 1994 Parsons Engineering Science, Inc. (Parsons ES), under contract with the Air Force Center for Environmental Excellence (AFCEE), conducted an SVE pilot test to collect cost and performance data on the ICE technology and to provide recommendations for the full-scale SVE system design. A full-scale SVE system using two 460-cubic-inch engines is now operating at a total volatile organic compound (VOC) removal rate of approximately 2,200 pounds per day, with a destruction efficiency exceeding 99.9 percent.

1.1 SITE HISTORY AND DESCRIPTION

The spill occurred at a jet fuel pumphouse consisting of nine 40,000-gallon and one 50,000-gallon underground storage tanks (USTs) containing JP-4 jet fuel, and an underground piping system that conveys the fuel to a fuel island. In 1985, a leak was detected in an underground fuel line, and an estimated 1.7 million cubic feet of soil were found to be contaminated with fuel. Jet-fuel contamination was detected in a soil column between depths of 8 and 260 feet. The groundwater is at a depth of approximately 300 feet.

From 1989 to 1993 remedial investigations and feasibility studies were completed under the U.S. Air Force Installation Restoration Program. The remedial alternative selected for the site included soil vapor extraction (SVE) followed by soil bioventing.

In 1993, an SVE pilot-scale test was performed by another contractor, and based on the results, a full-scale SVE system was designed. This design consisted of a series of 28 vapor extraction wells, a blower system, moisture separator, thermal oxidizer and catalytic oxidizer air treatment systems, propane tank, and associated piping and controls. The system was designed to operate at a maximum flow rate of 3,000 standard cubic feet per minute (scfm) with an operation period between 4 and 6 years in the SVE mode, then 2 years in a bioventing mode (at low rates of air injection). The construction/installation cost was estimated to be \$1.72 million, with an operating cost of \$23,400 per month for 4 to 6 years, for a total remediation cost of between \$2.84 and \$3.40 million (not including the 2-year period of bioventing treatment).

Because of the high cost for full-scale SVE treatment using thermal/catalytic oxidation, AFCEE contracted with Parsons ES to review alternative treatment technologies, including bioventing and the use of an ICE for vapor extraction and treatment. Results from a one-year bioventing pilot test indicated that biological degradation rates were too slow (10 to 50 mg/kg/yr) to remediate the highly contaminated soils (Parsons Engineering Science, Inc., 1994). Following the bioventing pilot test, SVE utilizing ICE technology was evaluated to determine the technical merit and potential cost savings of this technology.

1.2 DESCRIPTION OF ICE TECHNOLOGY

Vapor extraction and combustion is an innovative technology that uses an ICE with advanced emission controls to extract and burn nonchlorinated hydrocarbon vapors from the vadose zone. Vapors are extracted from the soil using the vacuum generated by the engine. The vapors are then burned as fuel by the engine. The exhaust gases pass through standard catalytic converters for complete oxidation before exiting to the atmosphere.

The ICE SVE system used at this site is equipped with an on-board computer system that provides the necessary monitoring for engine control. The 16-channel data reporting system monitors the engine's oil pressure/temperature, coolant temperature, exhaust temperature, exhaust percent oxygen, and engine speed and performance (extraction flow rate, inches of vacuum, supplemental fuel consumption, air/fuel ratio, and engine hours).

External electrical power is not required for this system because the electronic ignition is battery-powered. The ICE unit is equipped with a cellular phone modem for remote monitoring and to make necessary adjustments to engine speed to optimize engine performance and minimize supplemental fuel consumption. The remote monitoring capability allows for adjustments to be made while the unit is operating.

1.2.1 Pilot Test Using the V2C ICE

VR Systems, Inc., of Anaheim California developed the Model V2C ICE used for the initial pilot testing at DMAFB. The model V2C ICE system is capable of vacuum extraction flow rates ranging from 0 to 50 scfm, depending on soil conditions and the hydrocarbon concentrations of the extracted soil gas. Because this site has multiple extraction wells (EWs) screened at different intervals, the objective of initial pilot testing was to collect the following data:

1. Flow rates and pressure (vacuum) response and vapor concentrations at each EW screened interval;
2. Soil gas TVH concentrations before and after treatment at the ICE unit;

3. Changes in soil gas oxygen, carbon dioxide, and TVH concentrations both in the extracted soil gas and at multi-depth monitoring points; and
4. Overall cost to install and operate the system.

Based on the 90 day pilot test it was determined that the Model V2C could operate at 20-30 scfm and remove 200 to 300 pounds of volatile organics per day from the soil. Destruction efficiencies of 99.9% were achieved. The cost per pound of TVH removed decreased from \$1.12/lb to \$0.49/lb over the 90 day test period. Based on these positive results it was determined that the ICE was a cost-effective technology for removing and treating fuel vapors from this site. However, a larger unit would be required to accelerate and expand the clean up of the entire site.

1.3 SELECTION AND DESIGN OF A FULL-SCALE ICE/SVE SYSTEM

The data collected during the initial V2C pilot test provided the necessary information for the design of a full-scale ICE SVE system. The primary objectives of a full-scale system included a higher vapor extraction rate, lower cost per pound of TVH removed, lower maintenance/operating costs, remote monitoring/optimization capabilities, long-term reliability, and effective treatment of the entire site at the maximum design flow rate.

First, it was recognized that if an ICE system was purchased rather than rented, the cost per pound of TVH removed would be even lower than during the initial pilot test. Second, selection of the larger VR Systems Model V4 was made for the DMAFB site because of the elevated TVH concentrations ($>40,000$ ppmv) and the full-scale flow rate (120 to 150 scfm) that was required to remove vapors from the entire contaminated soil volume. The VR Systems Model V4 was also selected because of its remote monitoring/optimization capabilities and expected destruction efficiency of over 99 percent.

A redesigned full-scale SVE system utilizing an ICE vapor extraction/treatment system was installed in July and August 1995. The system included six vapor extraction wells completed at varying depths to focus vapor extraction in the most contaminated soil intervals, an ICE vapor extraction/treatment unit, a moisture separator, supplemental fuel propane tank, and associated piping and controls.

Well design and spacing were determined based on air permeability testing results, and flow rates were determined based on results of ICE pilot testing conducted from May to August 1995. The effective treatment radius for the full-scale ICE SVE system was determined based on radius of pressure response and changes in soil gas chemistry. Long term pressure response and soil gas monitoring indicated that the radius of influence from a single vent well exceeded 170 feet at a flow rate of approximately 20 scfm. During the bioventing pilot test, pressure response measured at a distance of 170 feet from the air injection wells exceeded 0.2 inches of water between 175 and 210 feet bgs (the depth zone with the most laterally extensive fuel contamination), and oxygen increases exceeded 10 percent. Pilot testing using an ICE confirmed that the vapor capture radius would exceed 170 feet at an air extraction rate of 20 scfm from each extraction well. ICE SVE pilot testing also indicated that initial flow rates exceeding 20 scfm from each extraction well could be maintained without the need for supplemental fuel (propane).

The vapor extraction wells used for the full-scale ICE/SVE system include the four existing wells installed for the initial SVE pilot testing and two additional wells installed in 1995. All extraction wells are constructed of 4-inch-diameter casing with stainless steel screens, and screened across soil intervals of relatively high fuel contamination and/or high permeability. The wells were screened at

various discrete intervals between 60 and 233 feet bgs. All six vapor extraction wells were separately valved and then manifolded at a common point so that flow rates from individual wells could be easily adjusted by a site remediation technician.

The full-scale design of the ICE/SVE system included a maximum flow rate range of approximately 300 to 500 scfm using two 8-cylinder ICEs. A moisture separator was installed in the piping between the wells and the ICEs. A 250-gallon propane tank was installed to provide fuel for the ICEs during startup and for periods when the soil gas total volatile hydrocarbon (TVH) concentration temporarily falls below that required for proper ICE operation.

The ICE/SVE system used at this site meets the stringent Pima County, Arizona air emission standards which require that TVH emissions not exceed 2.4 pounds per day (lb/day). Based on laboratory analytical results for the ICE exhaust samples, emissions over the first 120 days have averaged approximately 0.54 lb/day.

1.4 PERFORMANCE OF THE FULL-SCALE SYSTEM

The attached table and figures provide the overall capital and operating costs as well as information on the cost per pound of TVH removed, and total pounds of TVH removed during the first 4 months of the V4 full-scale operation. Table 1 shows how the daily ICE/SVE operating costs were derived and compare these costs to the estimated cost of SVE using thermal oxidation for vapor treatment. During the first year of treatment, the ICE will average \$0.065/pound of fuel removed compared to an estimated \$0.77/pound for SVE with thermal oxidation. During years two to five, the increased use of supplemental fuel will increase the ICE's daily operating cost. However, throughout the life of the project, the ICE will maintain at least a seven-fold cost advantage over the SVE/thermal oxidation option.

Figure 1 shows the total mass (in pounds) of TVH removed over time during the first 4 months of V4 operation. A total of 255,318 pounds of fuel were removed and treated by the V4 ICE system during the first 120 days of full-scale operation.

Figure 2 shows the cost per pound of TVH removed over the initial 120-day period. The actual cost per pound of TVH removed and treated by the ICE ranged from 6 to 7 cents. This dramatic decrease in treatment cost over the initial pilot testing period using the V2C was due to the large increase in total mass removed when compared to a relatively small increase in daily operating costs. Eliminating the need for an electrical power hookup and having remote monitoring capability has also proven to be a significant cost savings.

During the initial 120 days of full-scale operation, 12 days of downtime occurred. All downtime was associated with a condensate/moisture collection problem. This problem was addressed by adding a larger water knock-out drum and by insulating the exposed piping. The overall uptime during the initial 120 days of operation was 90 percent. No mechanical ICE system failures occurred during this period.

1.5 SUMMARY

The VR Systems ICE SVE unit has provided very effective off-gas treatment for fuel hydrocarbons. To date, the Model V4 system has proven to be reliable, versatile, and cost-effective while removing over 255,000 pounds of fuel during the first 120 days of operations. The system has consistently

TABLE 1
CAPITAL AND OPERATING COST COMPARISON
BETWEEN ICE AND THERMAL/CATALYTIC OXIDATION
SVE SYSTEMS AT SITE 35, DAVIS-MONTHAN AFB

	VR Systems Model V4 ICE ^{a/}	(Conventional) Thermal/Catalytic Oxidation SVE System ^{b/}
<u>Capital Cost</u>		
Includes:		
Treatment Unit (includes engine rebuild)	\$85,000	\$354,000
Extraction Well Installation	\$32,000	\$666,000
Extraction Blowers	NA	\$124,000
Design/Labor/Installation (includes contingency and profit)	\$45,000	\$580,000
 Total Capital	 \$162,000	 \$1,724,000
 <u>Operating Cost (daily)</u>		
Includes:		
• Capital [averaged over an estimated 5 year cleanup period (1,825 days)]	\$89	\$944
• Maintenance/Monitoring (includes monthly O&M and system sampling)	\$57	\$236
• Supplemental Fuel (daily) (includes propane and electricity)		
Year 1	\$0	\$544
Year 2	\$34	\$544
Year 3	\$68	\$544
Year 4 and 5	\$102	\$544
 Total daily cost (Year 1)	 \$146	 \$1,724
 Total pounds TVH Removed/day (Year 1) ^{c/}	 2,235	 2,235
Total Cost/pound (Year 1)	\$0.065	\$0.77
Total Cost/pound (Year 5)^{d/}	\$1.11	\$7.73

a/ Cost based on actual purchases and labor by Parsons ES.

b/ Cost based on estimate supplied to Air Force by other contractor.

c/ Assumes that thermal/catalytic unit is limited to influent of 8,000 ppmv TVH for safe (non explosive) operation.

d/ Assumes 10-fold reduction in soil vapor concentrations by Year 5.

Figure 1
Total Pounds of TVH Removed
During Initial 120 Days of V4 Full-Scale Operation

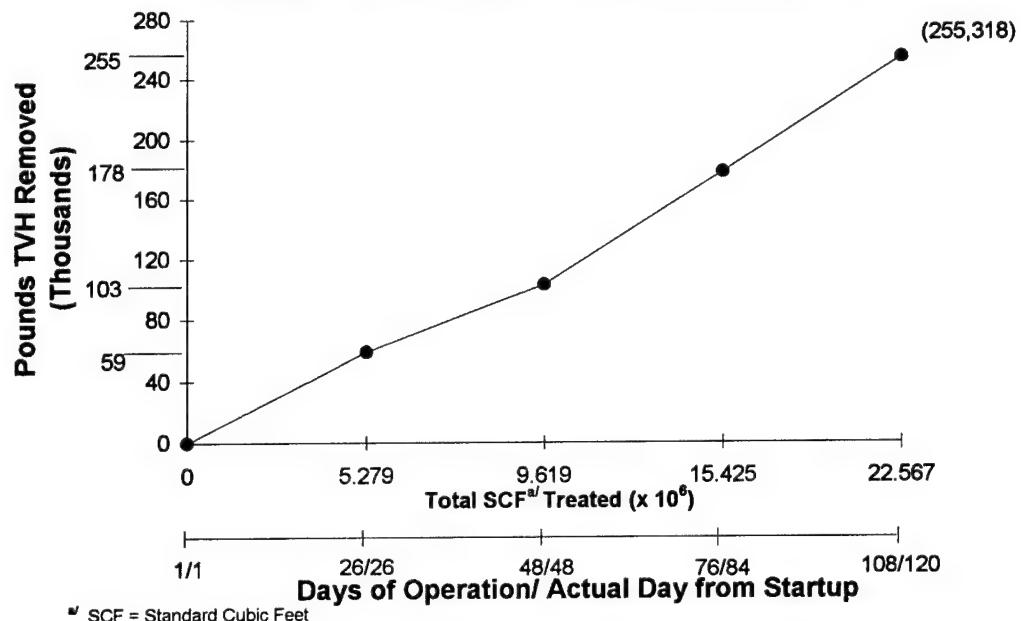
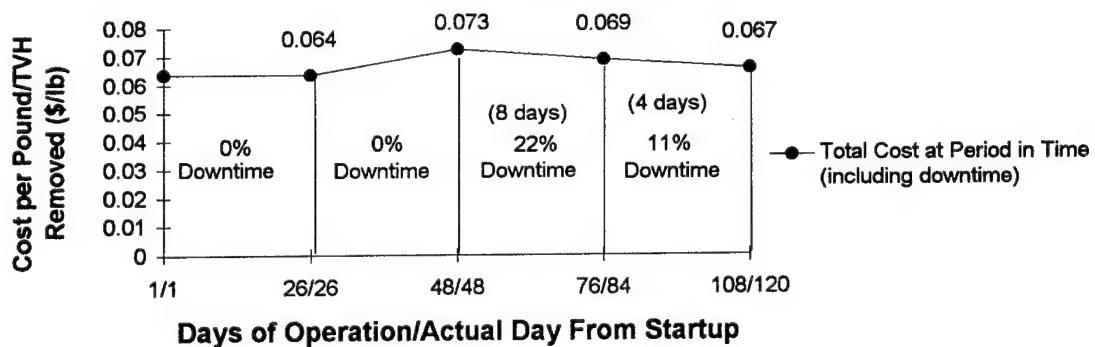


Figure 2
Actual Cost per Pound of TVH Removed
During Initial 120 Days of Full-Scale Operation Using the
V4 ICE SVE System



achieved hydrocarbon destruction efficiencies of greater than 99.9 percent and remained in compliance with one of the nation's most stringent emissions standards.

1.6 FUTURE WORK

This technology has made significant advancements over recent years. VR Systems is currently fabricating a remotely monitored automated valving and flow rate monitoring system for this site so that the flow from individual extraction wells can be blended to provide optimum engine performance and minimum supplemental fuel use. The addition of remote valve controls should reduce technician site visits and labor hours associated with onsite system optimization at sites with a multiple extraction wells.

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WATER

APPLICATION OF AN AUTOMATED FISH BIOMONITORING SYSTEM AT OLD O-FIELD FOR CONTINUOUS ACUTE TOXICITY EFFLUENT MONITORING

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ABSTRACT

An Automated Fish Biomonitoring System was developed by the U.S. Army Biomedical Research and Development Laboratory (USABRDL) to identify developing toxic conditions in water by continuously monitoring the ventilation and movement patterns of the bluegill (*Lepomus macrochirus*). Physiological stress to the bluegills, characterized by changes in fish ventilation and movement patterns, is used as an early warning to identify developing acute toxicity of a treated groundwater (effluent) discharge at Old O-Field, Aberdeen Proving Ground, MD. An IBM compatible personal computer continuously monitors and records ventilatory rate, ventilation depth, cough rate, and whole body movement of up to 32 fish simultaneously.

Monitoring begins with 16 fish held in control water for a three-day acclimation period followed by four days of baseline data collection. The fish are then divided into two groups (8 fish in control water and 8 fish in effluent). During the subsequent continuous exposure to effluent, the computer provides immediate analysis of statistically significant departures from baseline conditions for fish in the control and effluent-exposed groups. After two weeks exposure to effluent, new fish are placed on-line to continue monitoring the effluent. The U.S. Environmental Protection Agency Region 3 included the automated fish biomonitoring system in a Record of Decision for the discharge of the effluent to the Gunpowder River.

The Automated Fish Biomonitoring System has been integrated with the Groundwater Treatment Facility at Old O-Field. When the monitoring system identifies a potentially toxic effluent (6 fish

responding to the effluent), an effluent sample is automatically collected for chemical analysis, a remote monitor in the treatment facility control room identifies the problem to the facility operators, and the discharge is diverted to storage tanks until the problem is resolved.

INTRODUCTION

The increasing use of biological approaches to evaluating water quality is illustrated by trends in regulating wastewater effluents over the last 25 years. Originally, chemical and physical measurements of effluent quality alone were considered sufficient for characterizing potential toxicity to aquatic organisms in receiving waters, but experience showed that some effluents that appeared nontoxic based on standard chemical measurements were nevertheless highly toxic to aquatic life. Consequently, laboratory tests with aquatic organisms are widely used in addition to physical and chemical measures to provide a direct measure of effluent toxicity¹. In addition, standard biological measurements have been developed for field evaluations of stream quality, including indices based on fish or invertebrate community structure². These measures offer a direct indication of toxicity and integrate the multitude of potential sources of toxicity that may be present. Even unsuspected and infrequent but highly toxic materials can be evaluated using biological approaches. One such biological approach is the monitoring of ventilatory response to environmental stressors. Ventilatory responses are often some of the first prelethal symptoms exhibited by animals to environmental stressors³.

The Automated Fish Biomonitoring System developed at USABRDL^{4,5} provides several additional biological measures that significantly increase the utility of the system as a biological monitor for developing acute toxicity of an effluent. The ventilatory system gives near real-time continuous toxicity evaluation which translates to near real time feedback to plant operations. The system gives an early warning to developing acutely toxic conditions leading to the prevention of acutely toxic releases to the environment. The ventilatory system has been automated to provide unattended and remote toxicity monitoring.

SITE BACKGROUND AND HISTORY

Old-O-Field is a 4.5 acre hazardous waste and ordnance disposal site located on the lower half of the Gunpowder Neck in the Edgewood Area of Aberdeen Proving Ground, Maryland. Surrounded by water on three sides (Watson Creek to the north and east, and the Gunpowder River to the west), Old O-Field is situated on a local topographic high with a 4 to 6 foot relief across the field. The site is mostly overgrown with small trees and scrub vegetation, with a few partially visible disposal pits.

Prior to its purchase by the U.S. Army in 1917 the site was mixed farmland and woodland, like much of the Gunpowder Neck Area. With the Army's purchase, the site became integrated into the Edgewood Arsenal, but disposal activities did not begin until the 1930s. During the 1940s and early 1950s, unlined pits and trenches were dug within Old O-Field and used for the disposal of military unique substances, munitions, contaminated equipment, and miscellaneous hazardous waste. Trenches were typically 12 feet deep, 20 feet wide, and covered with soil. No disposal appears to have been performed after 1953.⁶

The Army has performed several cleanup operations at Old O-Field. In 1949, a decontaminating agent was applied to the field to detoxify mustard agent that had been scattered over the area. However, recent analyses of Old O-Field groundwater have revealed chlorinated hydrocarbons that probably resulted from the decontamination effort. The early attempts at cleanup resulted in further contamination of Old O-Field groundwater. In 1953, another cleanup operation was conducted which involved soaking

the field with fuel oil and allowing it to burn for several days. Further decontamination and cleanup efforts were limited to removing and securing ordnance items recovered in surface sweeps across the field. Currently, the site contamination is being controlled by the installation of a permeable cap and a pump and treat system to remove the contaminants from the groundwater prior to entry into the Gunpowder River.

GROUNDWATER TREATMENT FACILITY

To address the problem of groundwater contamination, the U. S. Army Department of Safety Health and Environment at Aberdeen Proving Ground has built a treatment facility which extracts groundwater and treats it by 1) chemical precipitation to eliminate heavy metals 2) air stripping to remove volatile organic compounds 3) ultraviolet oxidation to chemically oxidize organic compounds, and 4) carbon adsorption to remove residual organic compounds that may not have been destroyed by the previous unit processes. The final effluent is monitored by an in-line continuous fish biomonitoring system to determine whether the effluent leaving the treatment facility is acutely toxic. Treated water is either discharged to the Gunpowder River, or passed through the treatment process again if the treatment has been found to be inadequate.

EFFLUENT DISCHARGE MONITORING REQUIREMENTS

The Record of Decision agreed upon by EPA Region 3 and Maryland Department of the Environment placed the following monitoring requirements on the Old O-Field groundwater treatment facility effluent for the first 2 years of operation. The effluent was to have routine sampling for chemical analysis (metals, volatile organic compounds, and mustard agent degradation products), quarterly biomonitoring using fathead minnows and ceriodaphnia, and the installation and operation of the Automated Fish Ventilatory Monitoring System.⁷

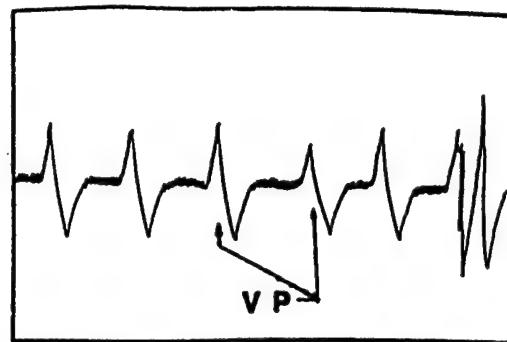
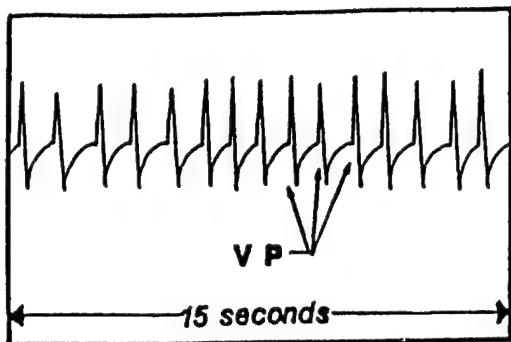
METHODS

TEST FISH

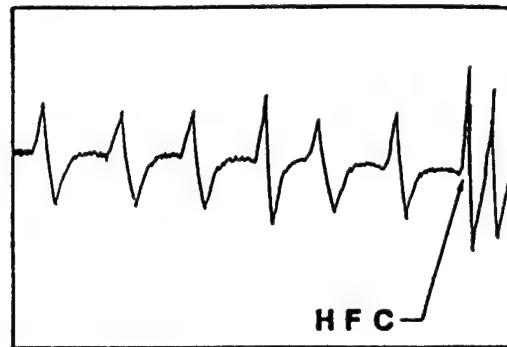
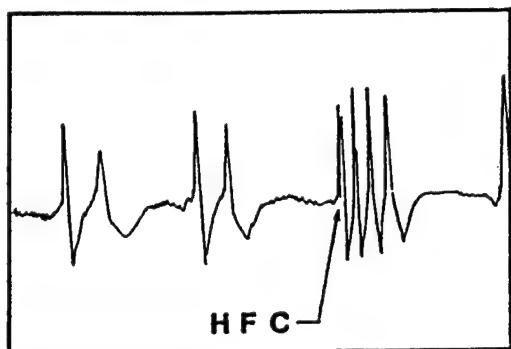
Bluegills, *Lepomis macrochirus* can be acquired from commercial hatcheries or field collected year round for use in the ventilatory monitoring system. The bluegills were placed on site, acclimated to continuous light and control water for a minimum of 2 weeks prior to testing. During acclimation and testing, wide spectrum fluorescent bulbs with a color rendering index of 91 were used. Testing was conducted under continuous light to eliminate diurnal changes in bluegill ventilatory patterns. During acclimation in the holding facilities, fish were fed Rangens #3 trout food (Zeigler Bros., Inc., Gardners, PA) plus frozen brine shrimp (Living World, Virginia Pet Supply, Fairfax VA). Fish were not fed during the 2-week effluent exposure period.

BLUEGILL VENTILATORY PARAMETERS

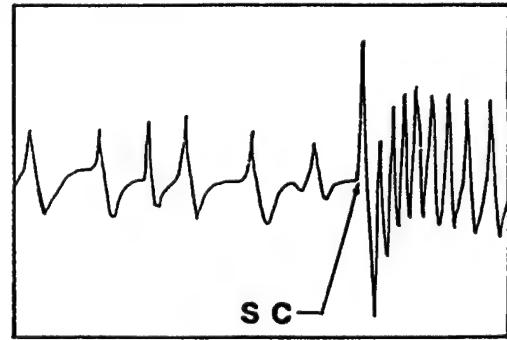
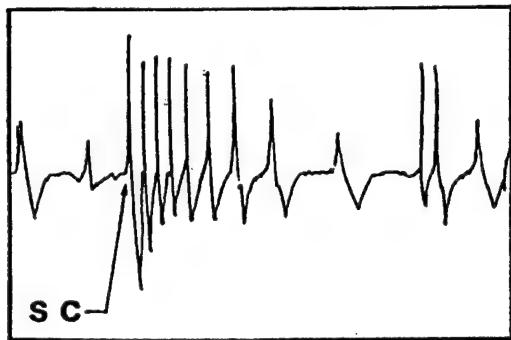
The monitoring system analyzes changes in the ventilatory activity of fish². The electrical impulses generated by muscular activity of the fish are amplified, filtered and analyzed to create a four parameter monitoring system. These parameters are: ventilatory rate, mean signal height (ventilatory depth), gill purge rate (coughs), and rapid irregular electrical impulses (whole body movement). Figure 1 shows typical ventilatory electrical signals from the bluegill.



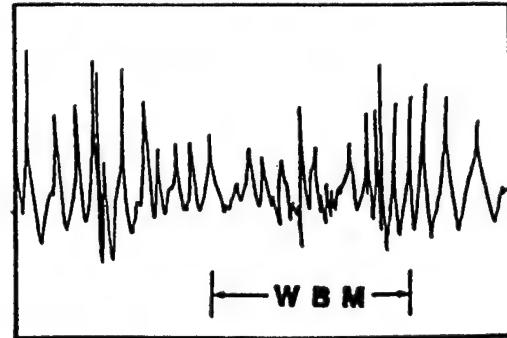
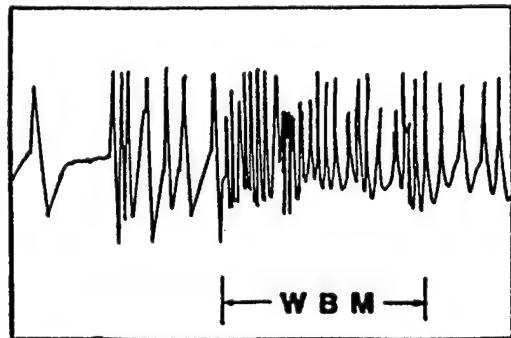
V P - VENTILATORY PEAK



H F C - HIGH FREQUENCY COUGH



S C - SPIKE COUGH



W B M - WHOLE BODY MOVEMENT

FIGURE 1. TYPICAL VENTILATORY SIGNAL RECORDINGS

EXPERIMENTAL DESIGN

The Automated Fish Ventilatory Monitoring System is a 21-day test that cycles new fish in for testing every 14 days; 3 days acclimation, 4 days baseline data collection, and 14 days monitoring (exposure) to the treated groundwater (see Figure 2). There were two effluent treatments and two control groups with 8 fish per treatment and control. Each of the 32 fish used in the test were placed into individual test chambers (See Figure 3). After one effluent treatment group and one control group have been monitored for 7-days, a second set of 16 fish are placed in effluent treatment and control groups. After the 7 day acclimation and baseline data collection for the second set of fish, they were placed on-line for effluent monitoring. The first set of fish were removed from the chambers, weighed, standard length measured, and placed in a holding tank for a 2-week observation period. Due to the exposed bluegills potential acclimation to the effluent, the fish were not re-used and were euthanized. The ventilatory electrical signal is picked up by the chamber electrodes that are connected to individual amplifier filter boards using shielded cable. Each fish ventilatory signal is then sent to a personal computer for analysis of ventilatory rate, depth, cough rate and whole body movement.

During exposure to the effluent, each fish ventilatory pattern was compared to its own baseline normal limits. If the exposure ventilatory pattern differed from the baseline pattern, the fish was considered "out of control". For a treatment to be "out of control", 6 fish in that group were required to be out of baseline limits⁸. The continuous ventilatory data collected was summarized and recorded on electronic media every 15 minutes during each monitoring cycle. The data was also sent to a host computer for remote data access. Data were then evaluated and archived at USABRDL. A solenoid dilution device was used to maintain a 50 ml/min. flow rate to all fish chambers.

WATER QUALITY MONITORING

Continuous monitoring of dissolved oxygen, pH, temperature, and conductivity were accomplished using a multi-probe transmitter (H-20, Hydrolab Inc.). The water quality data were directly imputed and recorded in the 15-minute biomonitoring records. When the fish respond to changes in effluent quality, a signal is sent to an automated sampler and an effluent sample is taken at the time of response. The sample was then preserved and held for future analysis.

RESULTS AND DISCUSSION

LABORATORY SYSTEM VALIDATION

The accuracy of the Automated Fish Ventilatory Biomonitoring System was established by comparing stripchart records (128, two and one half minute records from six tests) to the computer generated values for ventilation rate, average ventilation depth, and cough rate. Whole body movement accuracy was not established due to infrequent movement events. The accuracy of the ventilatory rate and average depth was 99% with an R^2 value of 0.997 (slope = 0.94) and a cough rate accuracy of 118% with an R^2 value of 0.781 (slope = 1.27).

Laboratory results of single compound testing have produced 0.5 hour response times for zinc and pentachlorophenol at concentrations near the 96 hour L for bluegills. Responses were similar to those reported by McKim et al.^{9,10}

AUTOMATED FISH VENTILATORY BIOMONITORING SYSTEM APPLICATION

This manuscript covers the operational period for the Automated Fish Ventilatory Biomonitoring System from June 23, 1996 to March 31, 1996 at Old O-Field. During this period, the data acquisition

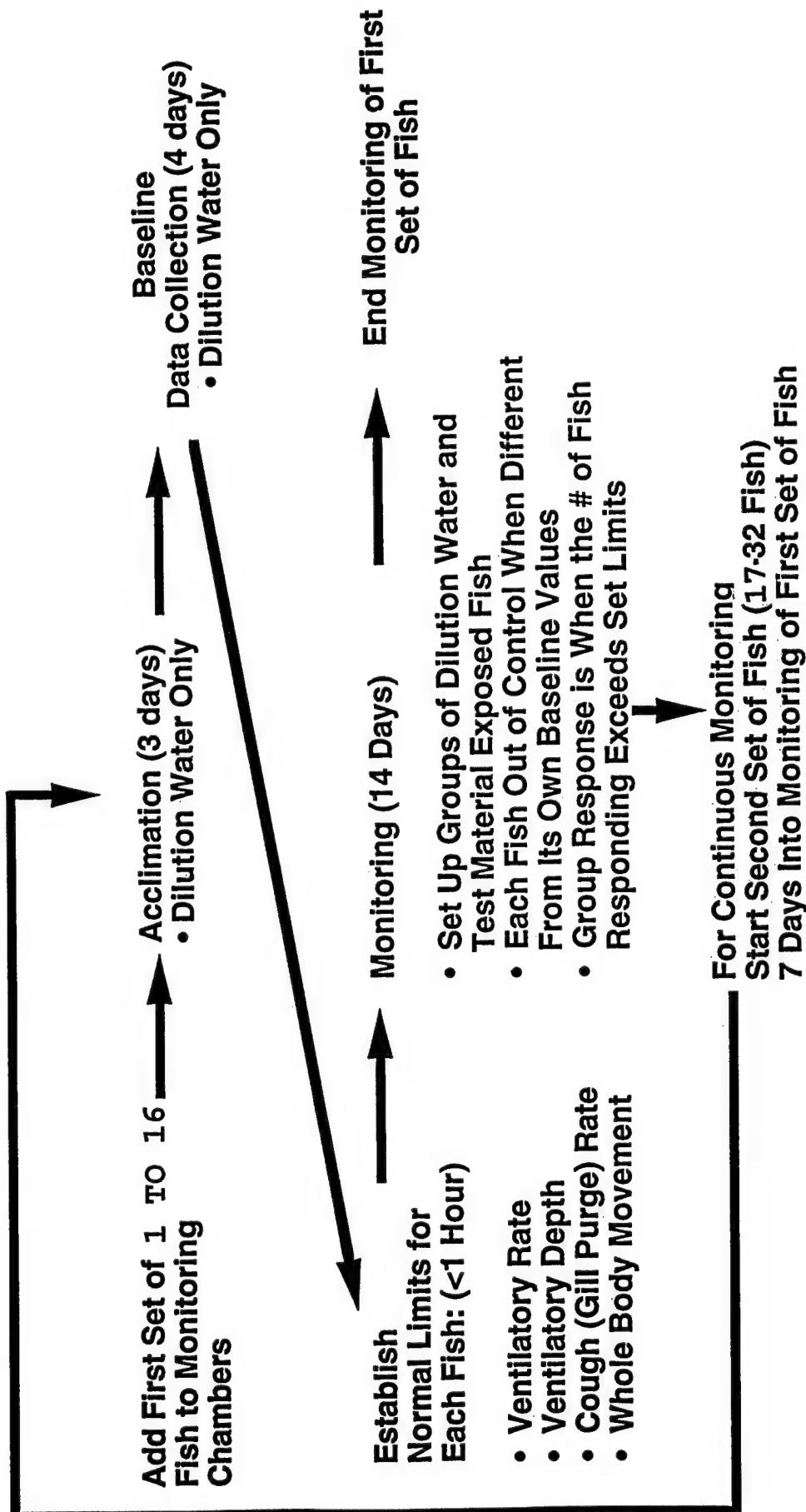


FIGURE 2. AUTOMATED FISH VENTILATORY MONITORING SYSTEM
Experimental Design

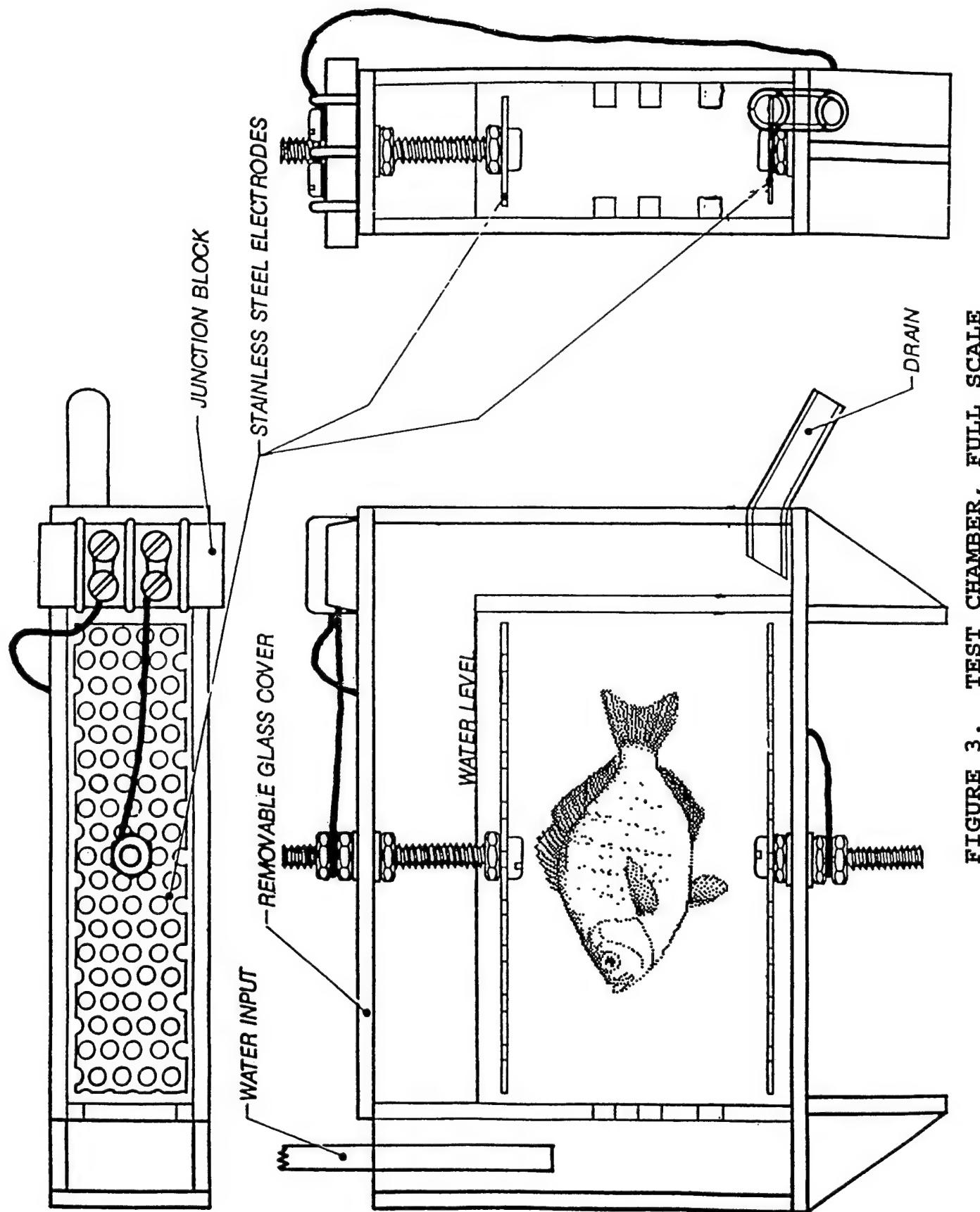


FIGURE 3. TEST CHAMBER, FULL SCALE

system was on-line for 273 days out of a total of 282 days. Data were not taken for approximately 9 days because the data acquisition system was off-line for various reasons (e.g., instrument calibration, data transfer, accidental program interruptions, power failures, etc.). No effluent discharge to the Gunpowder River occurred if the data acquisition system was off-line. No fish mortality was observed during discharge to the Gunpowder River as a direct result of groundwater process failure. This result was in part due to the early warning provided by the Automated Fish Ventilatory Biomonitoring System to the treatment plant operators. In most cases, corrections to effluent quality were made prior to the conditions becoming acutely toxic. However, acutely toxic conditions were identified during treatment plant maintenance and operational modifications were started.

A number of out of control responses occurred during the operational period. The total number of days the system obtained out of control responses was 21 days when the system was on-line. An explanation for the out of control responses was available for 20.6 days of the 21 days. No obvious explanation was apparent for 0.4 days. Since analytical samples were automatically taken when these responses occurred, analytical results of the preserved samples may provide additional explanations for fish ventilatory responses to the effluent.

ACKNOWLEDGEMENTS

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DISCLAIMER

The views, opinions, and/or findings contained in this manuscript are those of the authors and should not be construed as official Department of the Army position, policy, or decision, unless so designated by official documentation. Citations of commercial organizations or trade names in this manuscript do not constitute an official Department of the Army endorsement or approval of the products or services of these organizations.

Research was conducted in compliance with the Animal Welfare Act, and other Federal statutes and regulations relating to animals and experiments involving animals and adheres to principles stated in the Guide for the Care and Use of Laboratory Animals, NIH publication 86-23, 1985 edition.

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FIBER OPTIC-BASED BIOSENSOR FOR ENVIRONMENTAL APPLICATIONS

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ABSTRACT

The NRL fiber optic biosensor is a device which measures the formation of a fluorescent complex at the surface of an optical fiber. Antibodies provide a mechanism for recognizing an analyte of interest and immobilizing a fluorescent complex onto the fiber surface. The fiber optic biosensor is fast, sensitive, and it permits analysis of hazardous materials remote from the instrumentation. Antibodies coated on the fiber are stable for up to two years of storage prior to use. A portable fiber optic biosensor has been developed which is able to monitor four fiber probes simultaneously. Quadruplicates or 4 separate samples can be analyzed with the multiple fiber system. The biosensor has been used to measure concentration of toxins, proteins, small molecules in the parts per billion ($\mu\text{g/L}$) range in under 10 minutes. The fiber optic biosensor is currently being applied for detection of explosives, pathogens, and toxic materials which pollute the environment. On-site TNT analysis of explosive contaminated groundwater and leachate samples has been demonstrated.

INTRODUCTION

A biosensor is a detection system which exploits the sensitivity and selectivity of a biomolecule (i.e. an antibody) for analyte recognition and incorporates that biomolecule into an optoelectronic device for signal transduction (1-3). The NRL biosensor employs immobilized antibodies as the recognition component on the exposed fiber optic core. Upon binding of the analyte of interest, a fluorescence signal is generated at the surface of the optical fiber and the signal is transmitted back to a photodetector. To limit sample preparation and assay washing steps, signal generation occurs within a 100 nm area surrounding the fiber core referred to as the evanescent wave. Quantitative results can be determined based on the fluorescent signal levels. The fiber-optic biosensor is described here in terms of the optical components, chemistry for protein immobilization, and assay development.

OPTICAL DEVICE

Initial assay development was performed on a laboratory breadboard device (4). Recently, a portable fiber optic sensor was developed in collaboration with Research International (Woodinville, WA). This device, the Analyte 2000, is small (6.5" x 4.5" x 3.5"), lightweight (2.5 lbs.), portable, operates on either battery or 110V, and is able to monitor four fiber probes simultaneously (5,6). It employs 635 nm diode lasers for excitation and photodiodes to collect the returning fluorescence signal. A jumper cable of variable length connects the device to the antibody-coated optical probe.

The distal or "business" end of the fiber probe receives intensive preparation. The 600 μm fibers are decladded over the last 10 cm to expose the fiber core which forms the sensing region. To prevent signal loss, a method for propagating the fluorescent signal nearer to the center of the fiber by

tapering the declad region with hydrofluoric acid has been developed (2). The geometry that yields the most power in the evanescent wave, the least excitation of bulk fluorescence, and the best propagation of emitted light is a combination taper (7,8).

ANTIBODY IMMOBILIZATION CHEMISTRY

Once the fiber is tapered, the antibodies responsible for detection are immobilized on the unclad surface of the fiber probe. As described elsewhere (9,10), the fibers are cleaned and coated with a thiol-terminal silane. A heterobifunctional crosslinker, which reacts at one end with thiol groups from the silane and at the other end with terminal amino groups on the antibody, is used to attach antibodies covalently to the fiber surface. Antibodies are routinely immobilized at 2 ng/mm² (2) with a capacity to bind large protein antigens at a ratio of 1 antigen per 4 antibodies. Antibodies immobilized using this procedure, maintain antigen binding capability after storage of almost 2 years.

ASSAYS

Three types of immunoassays are being developed for use with the fiber optic-based biosensor for environmental applications. These assays include those specific for small molecules, proteins, and bacteria (11). In all of these assays, signal generation begins immediately upon introduction of the probe into the solution containing the fluorescent reagent. Fibers coated with irrelevant antibodies are used to control for false positive signals.

The main environmental assay with this biosensor is a competitive immunoassay which is used for the detection of small molecules such as explosives. In this assay, the analyte of interest (i.e., TNT) competes with a fluorescently-labeled analog for binding sites on the immobilized antibody. In this assay, an inhibition of the fluorescent signal indicates the presence of the analyte. The percent of inhibition is proportional to the concentration of the analyte of interest. The explosive TNT can be detected at low ppb levels with this system (12,13). With the TNT assay, the fiber probe can be used multiple times by removing bound analyte with 50% ethanol. This permits multiple samples and the reference samples without TNT to be analyzed on the same fiber. To demonstrate the performance of the fiber optic biosensor with environmental samples, detection and quantification of TNT in groundwater and leachate samples were performed at Umatilla Army Depot (Hermiston, OR) and Naval Submarine Base Bangor (Bangor, WA). The results from the fiber optic biosensor correlated well with splits analyzed via U.S. EPA SW-846 Method 8330 in a laboratory.

For detection of larger molecules, such as proteins and bacteria, a sandwich immunoassay was developed where the analyte of interest is bound between the immobilized antibody on the fiber and fluorescently-labeled antibody in solution (11,14). The increase in the fluorescent signal is proportional to the concentration of the analyte. Sensitivities of 1-10 µg/L have been obtained for several protein toxins including *Staphylococcal enterotoxin B*, ricin toxin, F1 antigen from *Yersinia pestis*, and endotoxin (6, 11,15). Several successful on-site analyses for the larger molecules have been performed.

A direct immunoassay can also be employed to detect bacteria (16). Cells are nonspecifically stained with a fluorescent dye. The cells are then exposed to the antibody-coated fiber optic probe. The cells of interest are bound by the immobilized antibody onto the fiber generating a fluorescent signal. As with the sandwich assay, the increase in fluorescent signal is proportional to number of cells of interest. The un-bound cells are located outside the evanescent wave and do not generate a signal. Detection of 3000 cells/ml have been achieved.

CONCLUSION

NRL has developed a portable fiber optic biosensor which can use long fibers for analysis remote from the optical components. The fiber optic probes are configured for homogeneous assays using the evanescent wave and the probe's geometry to significantly improve the signal transmission back up the fiber. Chemistry for immobilizing protein onto the fiber that successfully immobilized a high density of functional molecules has been developed. Antibodies can be immobilized on the fiber up to two years before use and remain functional. A wide variety of environmental assays has been developed which transduces a binding event into a fluorescent signal. Small and large molecules and pathogenic organisms have been detected in less than 10 minute. This biosensor has successfully analyzed samples on-site for TNT, protein toxins, and bacteria.

NOTES AND ACKNOWLEDGMENTS

Five patents (7,8,10,15,16) have been filed covering this technology and are available for license. The work would not have been possible without support from the Office of Naval Research (ONR), the U.S. Naval Medical R&D Command, the Environmental Security Certification Program (ESTCP) and Advanced Research Program Agency (ARPA). The authors particularly thank Brian Donner, Mark Pease, Joel Golden, George Anderson, Daya Wijesuria, Robert Ogert, Richard Thompson, and Carl Villaruel for their critical scientific contributions. The views expressed here are that authors own and do not reflect policy of the U.S. Navy, Department of Defense or United States Government.

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Dissolved Oxygen Management for Improved Wastewater Treatment

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ABSTRACT

Biochemical reactions for wastewater treatment are primarily reactions enabled by microbial metabolic processes. Waste treatment technology seeks enhancement of the reactions through environmental controls, dissolved oxygen levels, and bacterial speciation. In general, the reactions that occur within aerobic systems mineralize carbonaceous material through oxidation and scavenge chemical nutrients while microbial systems of anaerobic conditions produce reduced chemicals for gaseous disposal. These ambivalent environments commonly exist in zones within water mass of natural water bodies but they can be created within contiguous zones of managed waste streams. On meso-scales of time and space, these environments may exist in many locations within a waste stream and change continuously as hydraulic and chemical loading varies.

Microbial population management for treatment optimumization is generally a feedback from control of chemical and physical parameters, although, accelerated population adjustments through culture-dosing to serve transient waste stream qualities is also a management option. Some environmental support for sustained population systems include dissolved oxygen (DO) concentration controls for different treatment objectives along a flow-path. Dissolved oxygen concentration is difficult to measure but optimum control is contingent on continuous measurements.

DO sensor failures caused by biofouling is a common problem in all low-level oxygen environments typical of wastewater streams, however, a new DO measuring technology developed by this author is proved to be practical for advanced wastewater treatment requirements and for strict oxygen management.

Introduction:

Dissolved oxygen (DO) concentrations are water treatment factors for carbonaceous and plant-nutrient chemicals and an important factor in waste-solid bacterial uptake. Although atmospheric contact provides some oxygen to support biochemical processes of treatment in waste streams, chemical reaction rates and the metabolic demands of microbial populations are usually larger than supply rates from the surface. However, aerating equipment operations and optimum control of oxygen availability is technically difficult because accurate oxygen

measurement over continuous periods is compromised by oxygen sensor fouling. This paper provides a review of oxygen dependent chemical and biological water treatment technology as an introduction to requirements for new dissolved oxygen management technology.

Recent assessment of eastern U.S. coastal-region natural water quality (U.S. EPA, 1995) identified significant flux of plant-nutrient chemicals from coastal watersheds. Therefore, new limiting requirements for plant-nutrient chemicals discharge are likely. Although polymers and waste-conditioning chemicals are commonly used in wastewater treatment, the relatively large volume of waste solids creates an undesirable solids disposal problem so biological processes are preferred. Oxygen management for biological waste treatment processes vary in different treatment unit-processes, oxygen requirements for solids treatment are different for organic waste chemicals, and management of oxygen levels is commonly required for cyclic changes in waste loading .

Oxygen parameters for solids treatment:

Carbonatious solids in wastewater create a Biochemical Demand (BOD) for oxygen through reactions that are enabled by bacteria. In general, organic materials are assumed to carry the bacterial inoculants by which they can be reduced and, eventually, a stream of waste-organics would be expected to carry the bacteriological speciation best suited to the stream environment and chemical constituents. However, relative to the time duration of waste within a treatment plant, the evolution of these bacterial populations is slow.

In treatment processing the water environment is managed to optimize the rates and completeness of treatment processes which, for waste-solids treatment, is primarily the control of the microbial populations for reduction and uptake. Within a treatment plant, bacterial populations reflect the characteristic organic materials in the plant through-put, although, bacterial-culture dosing can be a tool for temporary adjustment to loading variations. Although the natural evolution of suitable bacterial populations would require relatively long time periods, accelerated waste reduction is possible through the inoculation of waste inflows with activated-solids. These solids are waste materials, cycled from the waste through-put, that have accumulated the bacterial conditions related to the contingent waste load. However, the inoculated input-loading with these solids results in stimulated chemical oxidation reactions, leading to locally depleted DO concentration, and oxygen demand (BOD) variation from cyclic waste-loading. This oxygen-chemical demand is seldom satisfied by less than continuous DO monitoring and automatic control of oxygenation through feedback from DO measurements.

A part of the treatment process is the separation of waste solids and bacterial colonies from the wastewater through gravitationally controlled settling. Although some solids settling difficulties are associated with physical parameters, most are biological and effected by dissolved oxygen levels. Zoogleal-type micro-organisms tend to form small clumps of solids; the largest of which have rapid settling rates. However at an extreme, large numbers of small particles are also formed which may be carried by transient flows through settling basins and outflows to produce unacceptable treatment quality by virtue of suspended-solids flow-through. At the opposite extreme, filamentous micro-organisms are associated with "bulking solids" which tend to the formation of large mats of solids. These solids masses tend to trap bubbles, to form floating masses that fail to sink, and to contribute to solids loss with the effluent flows. Since zoogleal organisms are growth limited at higher dissolved oxygen levels than at levels where filamentous populations are limited, oxygen level management may be used as a control

of solids settling rates. In practice, a microbial population between these extremes is desirable.

In a particular case, where dissolved oxygen concentration came into importance for solids control, small amounts of activated solids were pumped to combine with in fluent to primary clarifiers in attempt to increase solids settling. The operations created pseudo-bioreactors out of clarifiers that resulted in increased solids separation rates initially but, from accelerated loss of oxygen during warm seasons, denitrification of sludge in the clarifiers caused subsequent resuspension of solids from nitrogen bubbles.

Oxygen parameters for BNR:

Biochemical processes in oxygenated environments are important for biological nutrient removal (BNR). A typical system of unit processes for BNR is illustrated by the Modified Ludzak-Ettinger process (Figure 1; Olsson, 1992). The initial anaerobic zone may include head-works processors and primary clarifiers. Further oxygen reductions for the environment of the follow-on anoxic zone forces denitrification reaction mitigation by heterotrophic bacteria. In the aerobic zone, nutrient-organic nitrogen chemicals are taken into microbial cells and ammonium-nitrogen is oxidized into soluble compounds that are amenable to reduction when recycled back to the anoxic zone. This arrangement of unit processes utilizes advantages of the low oxygen content of inflows as inflow to the anoxic zone. Placement of the aerobic zone upstream of the final clarifier typically improves solids-settling and lowers suspended solids in effluent. As diagramed, cycling of activated solids supplies conditioned microbial populations of heterotrophic bacteria for improved nitrified-compound reduction. The biochemical nitrification rates are highly dependent on DO levels with limiting DO levels as high as 2.5 mg/liter for attached and suspended colonies. The reaction rates are also dependent on temperature, doubling over 10 degree C temperature ranges. A consequence of less than opportune conditions for these reactions is the resulting necessity for longer retention periods and proportional increases in facility holdings for the appropriate retention periods.

The attached microbial films on reactive surfaces in trickling-filter units also require well oxygenated surfaces for organic-nitrogen uptake and nitrification but management of air supply to the filters is partially dependent on parameters of the filter so, aside from the generalities of oxygen supply requirements, trial and error tuning of air supply is required. Greater control of oxygen is possible with use of suspended microbial colonies and, under low oxygen level environment, the same microbial populations that mitigated nitrification may be utilized to strip oxygen from nitrates and denitrify waste through release of nitrogen gas. With improved oxygen monitoring and automatic controls on oxygenation based on feedback from oxygen measurements, zonation of plug flow with regard to oxygen level is practical.

Many existing treatment plants use aeration as a means to locally mix waste streams, an operations practice which came from the relative inefficiency of oxygenation. Since large air volume pumping into waste streams is necessary for oxygen supply, the resulting mechanical agitation of the waste eliminated need for addition mixing. However with treatment targeted to the removal of selected waste chemicals, such requirements as oxygen management become important and the requirements lead to use of mechanical mixing in operational practice. This use of air-forced mixing has lead to maximal power usage in activated-sludge reactors because air bubbles used to force mixing is inefficient.

Improved oxygen monitoring:

To address the developing need for accurate and dependable dissolved oxygen measurement, the author with Science Applications International Corporation developed prototype oxygen monitoring instrumentation which has demonstrated a potential for service in the waste treatment industry. This new technology utilizes biological-fouling control to extend operational life of DO sensors in continuous deployment.

In recent years, high-quality DO sensors have become available on the commercial market which provide reliable measurements during continuous deployment within fully oxygenated surface regions of biological reactors. However these sensors foul rapidly in low oxygen environments and, with the resulting loss of calibration, measured DO becomes unreliable for automatic oxygenation controls. The new oxygen monitoring prototype deployed in the Haddenfield, New Jersey activated-sludge wastewater treatment plant operated with sensor fouling control for one DO sensor and with an unprotected oxygen sensor. As indicated from Figure 2, no change in the fouling-protected sensor calibration was evident during the seven week deployment based on the comparison of sensor measurements with chemical quantitative analysis. A graph of DO measurement differences between the measurements collected from the sensor with fouling protection and measurements from the unprotected sensor (Figure 3) indicates the effect of sensor fouling. After about seven weeks, the differences in measurement between the sensors is about 4.5 mg/liter.

Summary:

Increased oxygen control that is necessary to meet wastewater treatment requirements expected in the future will not be achievable with presently available DO sensor systems. These controls must come from automatic operations of wastewater treatment systems with control based on the properties of the waste stream itself.

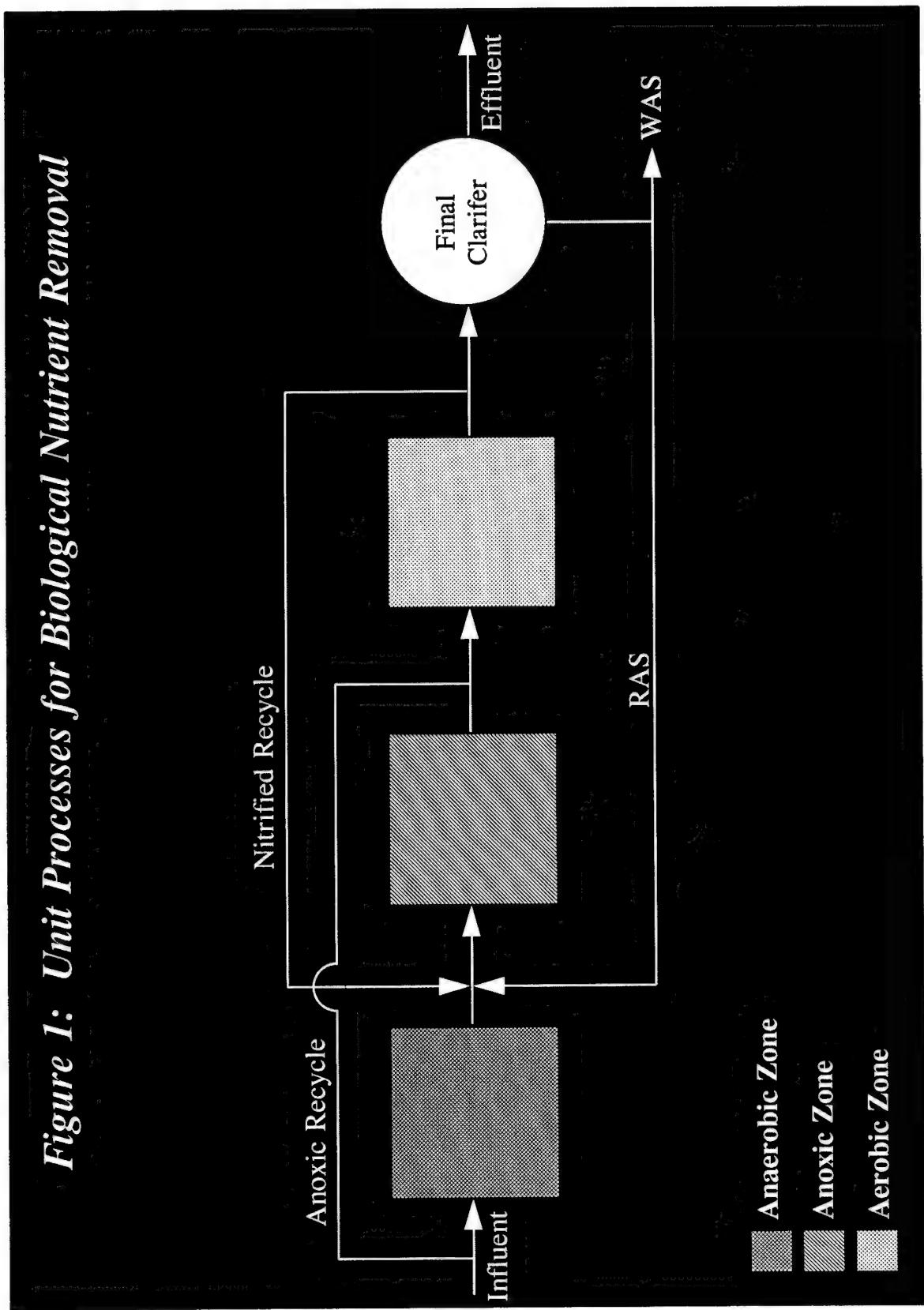
Oxygen measurements by the prototype DO monitoring system showed the new technology is capable of managing oxygen over practical periods of waste treatment operations and over maintenance-free periods that are acceptable by the treatment industry.

The degree of control of oxygen that is afforded by the new monitoring technology permits further investigation of other factors of biochemical control. This paper has included explanation for microbial control and chemistry that may be managed through optimumal treatment environments with oxygen and one can expect that other controls through other factors such as hydraulics, ionic conditions, temperature etc. can lead to further improvements of waste treatment.

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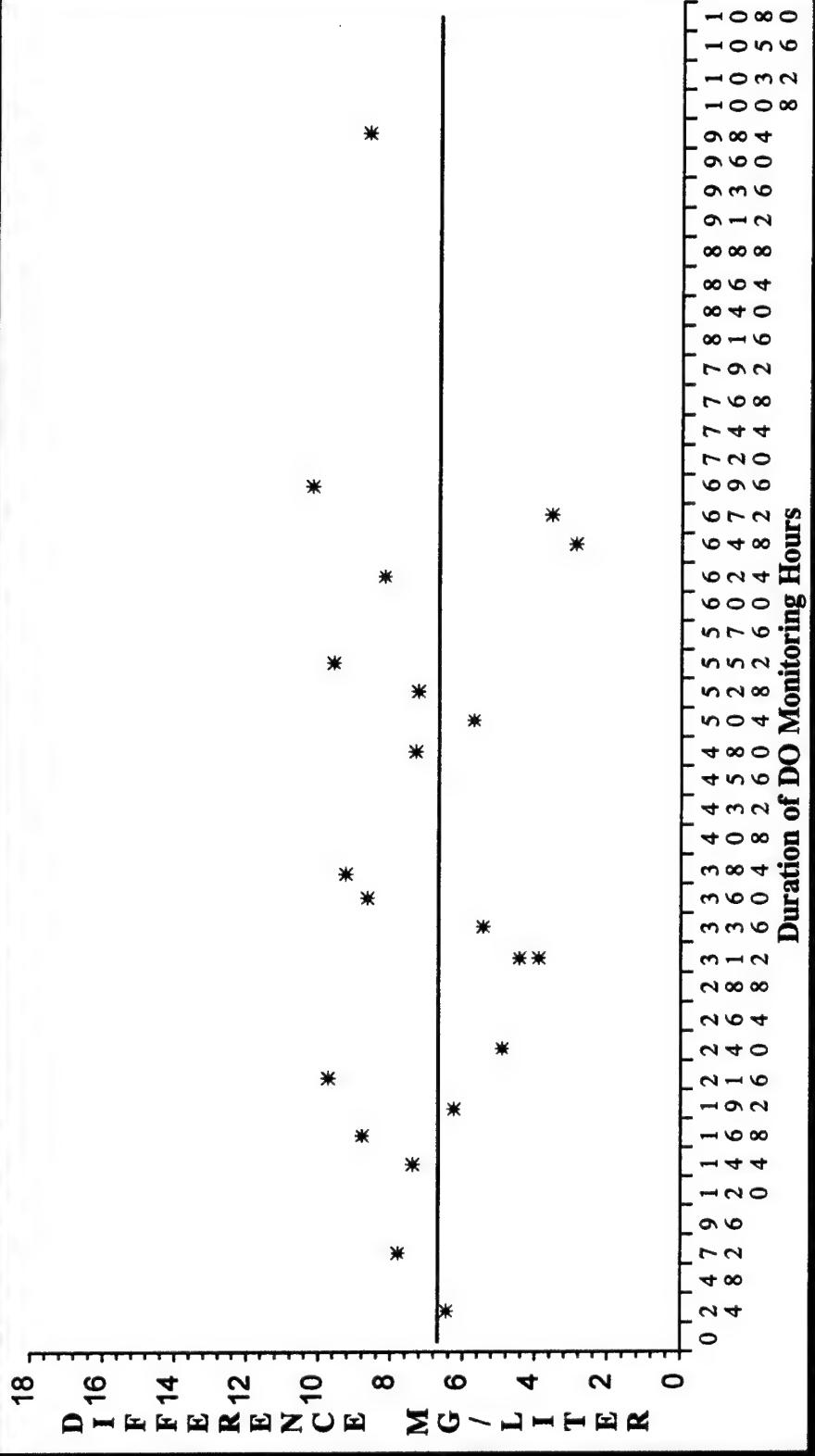
Figure 1: Unit Processes for Biological Nutrient Removal



Dissolved Oxygen Measurements

Ridgewood, NJ WWTP Summer 1994 Differences, Protected-Chemical Measures

**Figure 2: Dissolved Oxygen Measurements by Sensor with Biofouling Control
Compared to Chemical Quantitative Oxygen Measurements**

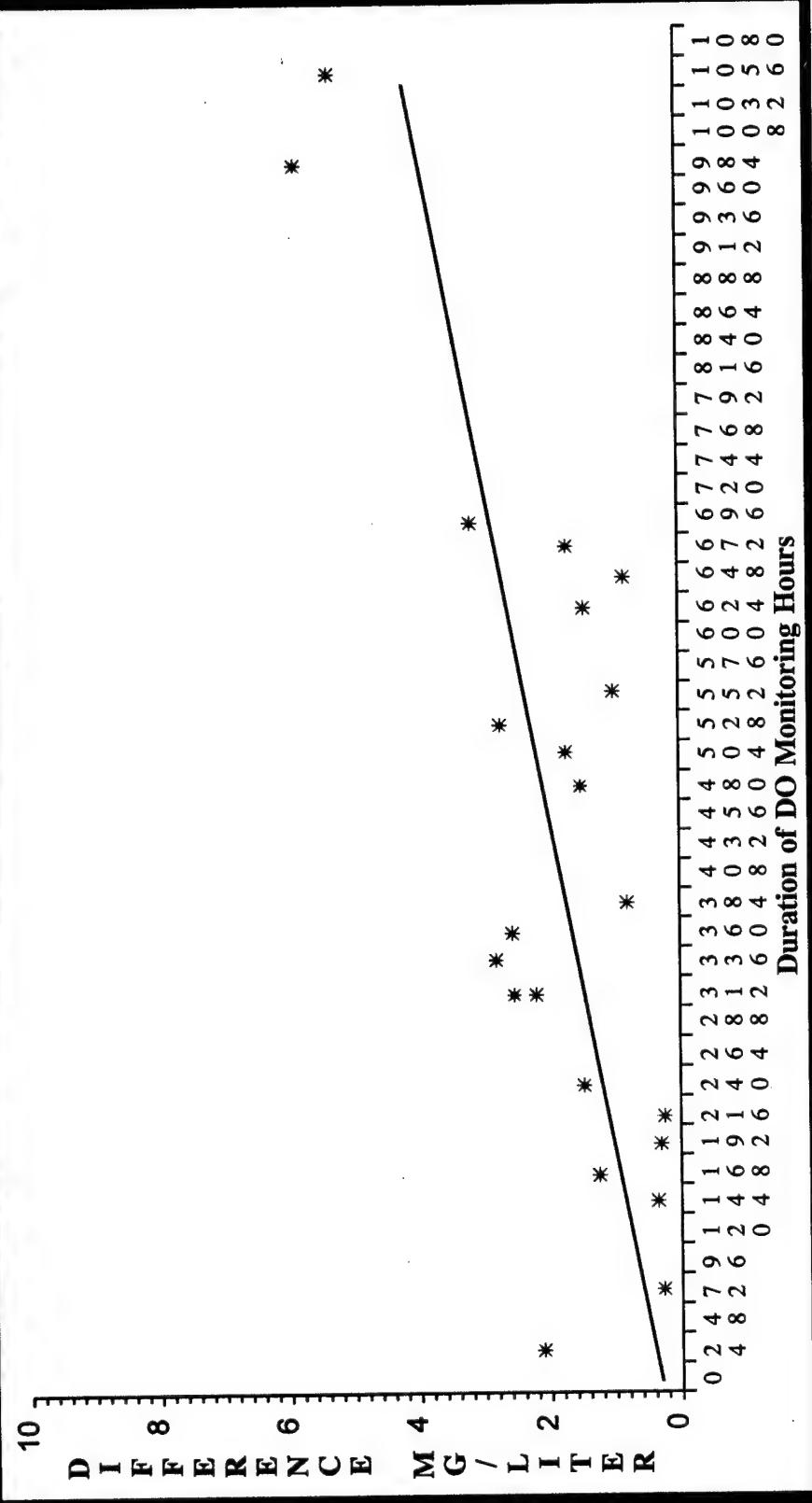


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Dissolved Oxygen Measurements

Ridgewood, NJ WWTP Summer 1994 Differences, Protected-Unprotected Sensors

Figure 3: Dissolved Oxygen Measurement Differences Between a Sensor with Biofouling Control and One Without Fouling Control



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A TOOLBOX FOR HEALTH RISK RELATED DECISIONS

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ABSTRACT

Development efforts since the late 1970s have resulted in a generalized method for ranking health hazards. This method provides the basis for a wide range of applications where decisions are needed for allocating resources on the basis of health risk considerations. It has been used for more than a decade to solve real problems and it is supported by 23 publications in the open literature. The diversity of this generalized methodology allows us to provide support in a great number of problem areas. We give four examples in this manuscript: (1) the relative toxicities of petroleum mixtures; (2) a method to derive Emergency Response Planning Guides; (3) an estimate of the possible carcinogenic potency of tungsten, an alternative material to depleted uranium for heavy armor penetrators, and (4) an approach to low dose extrapolation. Our experience suggests that many more applications of the original concept and variations on it can be of utility in military situations. Some potentially fruitful areas may be in the: development of a health-risk-ranking system for alternative solutions to manufacturing, waste management, and remediation; provision of a basis for identifying levels of hazardous agents which are below health concerns, or which should be of concern; development of a framework for evaluating chemicals and radioactive materials on the same basis, and in the development of a battery of *in vitro* bioassays which could take the place of long-term whole animal tests.

INTRODUCTION

Imagine that it could be possible to rank the toxic potency of a list of chemicals from least to greatest potency. Each chemical would be related to each other by a numerical assignment based on their potency. If one of the chemicals in the list were chosen to be the focal point for normalization, each chemical could, in principle, be assigned a multiplicative factor relating its potency to the potency of the "reference" chemical. The Environmental Protection Agency¹ recently found it useful to work in the context of this paradigm in order to estimate "toxic equivalency factors" for the class of materials known as dioxins. The many dioxin congeners are assigned equivalency factors relating each one to the most highly studied congener, 2,3,7,8-TCDD. This same concept can be applied to the hundreds or thousands of chemicals to which humans are now exposed. Our developments in this area preceded the recently coined term "toxic equivalency factor" but this term accurately describes both the concept and the working process which began development in the late 1970s.

The initial development of our process began during the era just after the oil crisis of the 1970s when the United States was exploring the production of synthetic fuels from coal. The first use was in the early 1980s in the Environmental Monitoring Plan for the U.S. Synthetic Fuels Corporation.² In this effort, the ORNL investigators were required to develop a method for identifying which and at what levels previously unregulated substances should be monitored: the genesis of the relative potency methodology allowed these questions to be answered. Within a few years after its introduction, the Rapid ASsessment of Hazard (RASH) method was established as being potentially useful in predicting new and/or changing regulatory criteria.³ Shortly after work was completed for the synthetic fuel program, the U. S. Air Force sponsored the development of the Hazard Assessment Rating Methodology (HARM) that finally became known as the Defense Priority Model for site-specific screening within the Installation Restoration Program.^{4,5} The human health portion of this HARM model was constructed by the ORNL authors around their earlier work on relative potency (toxic equivalency factor) methods. Later, in 1991, the relative potency methodology was used to predict the outcome of 42 substances which were to undergo long-term cancer studies by the National Toxicology Program. This methodology was highly successful in its predictions.⁶

METHOD (SCIENCE-BASED RISK MEASURES)

Starting with the fact that neither epidemiologically-based nor laboratory-based cancer studies were available for the complex process chemicals involved in the production of synthetic chemicals in the 1970s, it was necessary to develop a methodology which could minimize the need for models and minimize the need for lengthy deliberative review periods. The approach, as developed at ORNL, is a **data-intensive, assumption-free** approach. This approach anticipates and removes some of the problems of uncertainty and minimizes the impact of other problems associated with the historical dose-response extrapolation models, especially when appropriate data are not available. An estimate of the relative potency (RP) of a test chemical "T" compared with a reference agent "R" can be obtained by comparing the doses (D_T and D_R) required to cause the same level of response in a particular biological test model considered to be relevant to the disease of interest. This process can also be thought of as producing toxic equivalency factors. An estimate of the relative potency is given by:

$$RP = (D_R/D_T).$$

The relative potency framework as utilized at ORNL involves a comparison of dose levels of different agents (chemicals) to give a common outcome in a common experimental protocol. These ratios of dose of reference agent to dose of test agent represent a distribution in sensitivity of the various test systems, which themselves represent a variety of species, strains, dosing methods, time course of dosing etc. Since nearly all of the biological test systems are "tuned" to be sensitive to some insult, the test systems should not be thought of as being individual surrogates for humans. Rather, they can be thought of as collectively representing the range of responses by living organisms. Not having information upon which to determine the underlying distribution of responses, the summary measure determined for use in this work is the median.⁷ The summary relative potency is then the median of the collection of relative potency ratios.

For evaluation of the role of mechanisms, we selected 52 carcinogens, primarily from the list of carcinogens published by the IARC.⁸ Long-term whole-animal data on tumorigenicity and short-term bioassay data were obtained from the Registry of Toxic Effects of Chemical Substances.⁹ To avoid any potential bias, 6 chemicals from among the 52 were chosen to serve as reference compounds. These 6 reference compounds were chosen to represent different mechanisms of action: Direct acting--Propiolactone: Indirect acting--

Dimethylnitrosamine; Epigenetic--Benzene, 2,3,7,8-Tetrachlorodibenzodioxin, Epichlorohydrin; and metallic Cadmium.

In determining whether or not mechanism of action was important for ranking the long-term whole-animal tumorigenic studies, 6 rankings of the 52 chemicals were performed.⁸ These 6 lists were compared with one another, two-by-two, for consistency using the Spearman Rank Correlation test. All of the 15 pairs which were ranked had Spearman Rho values of 0.8 or greater and p-values were typically less than 0.0001. These results provide a high degree of confidence that the relative potency framework, as used, can be expected to reliably rank toxicologic potency using long-term whole animal studies regardless of the mechanism of action of the agents being ranked.⁸

In an attempt to push the relative potency concept to the limit, it was subsequently evaluated using only short-term tests.¹⁰ Short-term tests involve bacteria, yeast, mammalian cells, and, sometimes, host animals. Despite this diversity, when relative potencies using data from short-term tests were evaluated for test chemicals with respect to a well studied reference chemical, a distribution of ratios was found similar to that for the whole animal tumorigenicity data. Using short-term data, the 6 reference chemicals were used to rank the 52 carcinogens, just as before. As might be expected, the range of responses (ratios) within the short-term assays was greater than within the whole-animal assays and therefore the median was less stable. As a consequence, when the 6 rankings of the short-term tests were compared with the 6 rankings of the tumorigenic tests using the Spearman Rank Correlation test, the correlations were lower than before. Correlation values were typically 0.4, and the p-values were higher, typically 0.01 to 0.05. Considering the fact that the individual ratios are based on mostly *in vitro* assays and that the ratios for a given test and reference chemical often vary by factors of 1,000,000 or more, the consistency of Spearman's Rho values (which can vary from -1 to +1) which generally varied between 0.35 and 0.6 is remarkable. Only three p-values of the 15 two-by-two pairs were greater than 0.05. They were 0.16, 0.08 and 0.06. Again, given the consistency of results and the summary statistic (tested against a two-tailed distribution), the strength of the correlation is remarkable. The short-term tests measure responses of widely varying biological systems to widely varying endpoints. Because of the consistency in ranking, confidence is gained that this methodology can be employed to rank essentially every occupational or environmental agent regardless what mechanisms are acting.¹⁰

A general form of this relative potency approach can be based on an indirect set of comparisons using a composite of slope factors for the epidemiologically-based studies on beryllium oxide, chromium VI, acrylonitrile, nickel subsulfide, coke oven emissions, nickel refinery dust, arsenic, benzene, cadmium, and benzidine. These same materials have extensive animal and cellular data which are used to provide a link with the fundamental reference, benzo(a)pyrene. Relative potency methodology, thus provides a link, by means of common bioassays, between a test chemical and benzo(a)pyrene, and between benzo(a)pyrene and the 10 materials listed above. The accuracy of the risk estimate for a test chemical then rests on the accuracy of the human risk based on epidemiological studies of those ten materials and the available data for the test chemical. The ten materials listed above were determined to have a carcinogenic slope factor of $4.7 \times RP$ (mg/kg-d)⁻¹ where RP is the potency of the test chemical relative to benzo(a)pyrene.³ Thus there can be a linkage between the epidemiologically-based cancer slope factor aggregated over 10 well studied materials and any material for which some bioassay data exists.

APPLICATIONS

RELATIVE TOXICITY OF PETROLEUM-BASED PRODUCTS

During the past two decades, a significant effort in toxicological research on petroleum-based materials has been supported by the United States Armed Forces. These studies have investigated effects on biological

systems from the complexity of the human being to the simplicity of *in vitro* assays. In order to eventually predict or characterize the potential human toxicity, detailed mechanistic studies have been pursued for a variety of biological endpoints including changes in metabolism, growth rates, overt toxicity, neurotoxicity, mutagenesis, carcinogenesis, irritation, hematology, behavior, and so on. Results of many studies have been used to provide exposure guidance to protect against specific occupational hazards or to provide guidance for military specifications designed to minimize specific hazards, yet successful attempts to provide a common toxicological framework for petroleum derived fuels and lubricants are not forthcoming. A major reason for this vacancy is thought to be the wide range of toxicological responses observed in some mixtures and the lack of clear evidence of toxicity in others. For example, often even large doses of some petroleum derived fuels, approaching a physical maximum, do not result in lethality in animal systems. We applied our methodology to a wide range of data types in order to demonstrate the potential usefulness of this approach.¹¹ Data for the mixtures to be described was derived primarily from U.S. Air Force sponsored work. Summary relative potency measures of the median and interquartile range are presented in Figure 1.

The petroleum-based materials under investigation fall into broad categories, varying from the lighter end of a distillate column to the heavier end. Often, additives to the distillate cut are provided to enhance certain desired characteristics. For a given supplier, the primary mixture varies as a function of origin of the crude feed stock and, to a lesser degree, operating conditions. Different suppliers also have different additives.

Hydraulic Fluids Hydraulic fluids include synthetic hydrocarbon-based materials and petroleum-based materials; both contained tricresylphosphate. Because these two types were similar in bioassay results, they were combined. The other hydraulic fluid was a water-glycol based fluid.

Gasoline, Stoddard Solvent, Jet Fuels, Kerosene, Diesel Fuel and Light Heating Oil These materials all come from around the middle distillate cut and just above. Stoddard Solvent, known also as mineral spirits is a mixture of straight and branched chain paraffins, naphthenes and alkyl aromatic hydrocarbons. Gasoline is primarily derived from high distillate fractions which have been reconfigured. Data for leaded and unleaded gasoline were combined and represent automotive fuel. Data for light fuel oil is from a low-catalytic cracked (10%) fraction. Most data found was for marketplace samples.

Heavy Fuel Oil, Diesel Fuel Marine, Lube Oil and Motor Oil These materials are all derived from a relatively higher boiling fraction. Heavy fuel oil and diesel fuel marine are similar except that diesel fuel marine must be clear and bright. Lube oils included paraffinic and napthenic oils. As data resulting from toxicologic tests was not significantly different among these oils, they were combined. Of the four samples of heavy fuel oil, the most toxic one was chosen (it also had the highest sulfur content).

EMERGENCY RESPONSE PLANNING GUIDES (ERPGs)

Sometimes it is necessary to identify an appropriate exposure level for an acute situation such as in planning for emergencies. The American Industrial Hygiene Association (AIHA) has been developing such guides, known as ERPGs.¹² These are being adopted by many organizations, but not all chemicals have been evaluated. We have applied the relative potency methodology for a subset of the chemicals for which there exist ERPG values. Results are presented in Figure 2. From this figure, it can be seen that a reliable slope is developed between the AIHA derived ERPG values and the relative potency values that we derived. This provides adequate confidence that screening levels for additional chemicals may be derived using the relative potency methodology (for data that may only include *in vitro* bioassays if necessary).

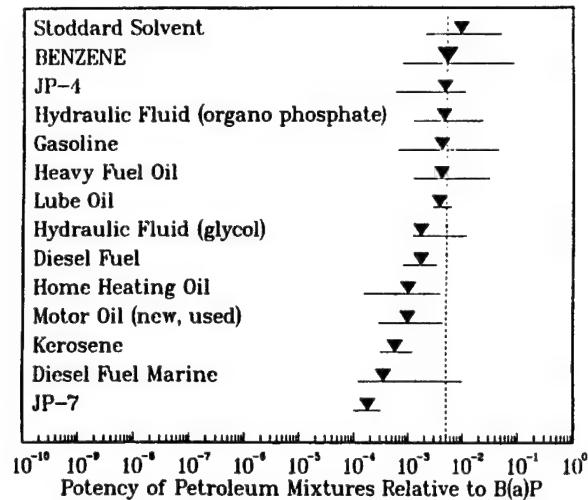


Figure 1. Toxicological potency of selected petroleum mixtures relative to benzo(a)pyrene derived using the relative potency methodology.

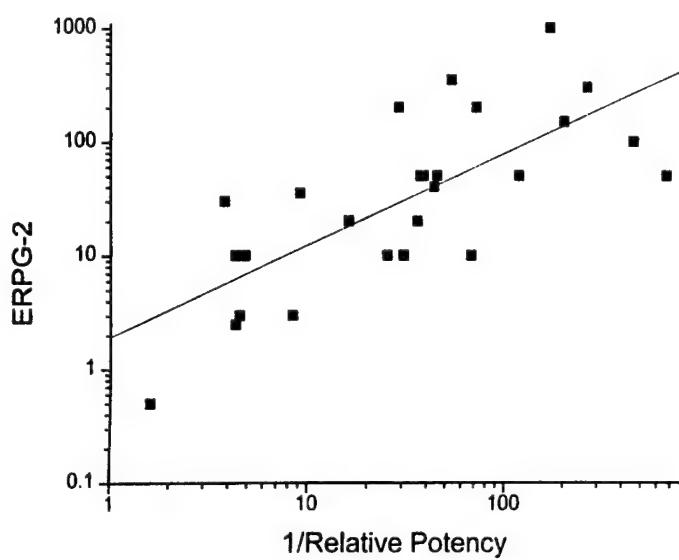


Figure 2. Inverse of relative potency plotted against the Emergency Response Planning Guide #2.

ALTERNATIVE MATERIALS FOR HEAVY ARMOR PENETRATORS

Several organizations within the DoD have an interest in learning whether or not there is a more environmentally benign material suitable for heavy armor penetrators than depleted uranium (DU). One of the more promising candidates is tungsten or a tungsten alloy. A major interest in the candidate materials is their potential to cause serious health impacts to soldiers deploying the weapons or to private citizens who live in the vicinity of where the penetrators are produced, used in practice, or disposed of. In investigating some of these questions for a U.S. Army sponsor, we found that there were no cancer studies in humans upon which to base a traditional analysis. Because there are no human studies clarifying the question of whether or not

tungsten is a carcinogen, and no laboratory animal studies of cancer upon which to draw, a non-classical approach was developed. The question to be asked had to be modified from "is tungsten a carcinogen?" to "if tungsten is found to be a carcinogen, what would be its potency?" Our experience in analyzing diverse forms of data was a key characteristic that allowed us to develop an answer to the question.

The sparse amount of data on tungsten was assembled and evaluated using five different reference compounds.¹³ Multiple reference compounds were necessary because it would have been impossible to use the majority of tungsten data with a single reference material because the overlap between any one reference compound and the tungsten data was not very great. Figure 3 contains plots of tungsten data compared with each of the five reference agents and then a combined plot for which all comparisons are normalized to the standard reference agent, benzo(a)pyrene which is defined to have a potency of 1.0. On the basis of the very sparse data, evidence from the combined figure suggests that the potency of tungsten, if determined to be a carcinogen, would be in the neighborhood of 0.04 relative to benzo(a)pyrene. This calculation of potency is based on a preliminary analysis, but it does provide important evidence and points the direction for important next steps in the evaluation program.

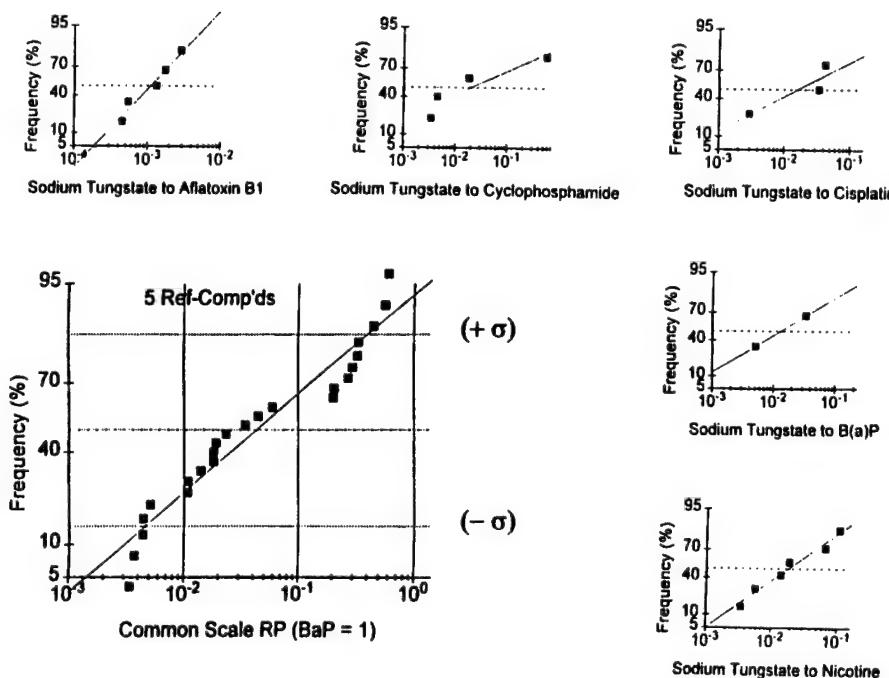


Figure 3. Relative comparisons between tungsten and five reference compounds. Contained in this figure are all the data identified on tungsten which could be relevant to the cancer endpoint, i.e. *in vitro* and *in vivo*.

LOW-DOSE EXTRAPOLATION

A fourth example of the types of problems that can be addressed by the general approach which we have developed is that of extrapolation of health risk data to situations in which the exposure of interest is well

below the exposure situation of the main body of data. Usually the risk measures, sometimes known as slope factors, are derived from either human epidemiological data of workplace exposures or from animal data in cancer studies. Both of these situations result in rather high exposures relative to the situation of interest in environmental matters. The question is how to best use these data taken at the relatively high exposure level: currently, simple linear extrapolation from the high-dose points is the method of choice. Based on our historical development, we have identified an improved approach. This process has not been developed to the point of application but we believe that all of the important conceptual foundation elements are present.

One of the driving forces for this low-dose approach is derived from the need to have the risks from a given level of exposure more accurate than we believe is presently available. With respect to cleanup levels in the environment, the cleanup standards imposed on industry are largely based on animal studies whose link to human health is the subject of debate. Modern research in molecular biology, genetics and DNA damage/repair mechanisms provides an opportunity to put the risk to humans and ecological systems on a rational defensible, scientific basis. If clean-up standards are much lower than the threshold at which human and ecological safety is at risk, then the cost to the DoD and other government agencies (the tax payers) can be needlessly high.

Our approach to low-dose extrapolation is improved by its focus on fundamental research topics such as molecular biology, genetics, cytokine production, and DNA damage/repair mechanisms to name a few. In addition to the break with the tradition of a nearly exclusive use of high dose animal carcinogenesis experiments, our approach is based on an encompassing parallel process so that the predictions of risk will be stable and not depend on single attributes like linear extrapolation from one or a few high-dose data points from carcinogenesis experiments, as is customary in the presently accepted approaches to low-dose extrapolation.

Three separate considerations are critical to address issues of low-dose risk: (1) the risk coefficients for most carcinogenic substances are reasonably valid for exposures that do not require low-dose extrapolation; (2) the **toxic equivalent factor** (our relative potency) concept as promulgated by the EPA for congeners of PCBs, dioxins and furans represents a generalizable process for defining exposure-rate effectiveness factors and dose-magnitude efficiency adjustments, and (3) the precise and accurate laboratory data on several biological structure levels can be analyzed in terms of frequency distributions. Table 1 provides a prototype of an approach to implement these ideas. In the conceptual approach, the biomarkers in the table are used to "translate" the data from higher dose animal and human data to the regime of lower dose. The concept of "data translation" here is similar to the "translation" methods developed and validated in the relative potency methodology described earlier. The difference is that, in our previous work, the bioassay data was used to translate information on one chemical to equivalent information on another chemical. In the low-dose extrapolation concept, the process would be one of translating human and animal response at a given dose to lower doses by using bioassay data on the same chemicals but at lower exposure levels.

Table 1. Illustration of how data-base analysis of biomarkers can be used to develop non-linear models of risk for human exposures. Squares indicate that data may be available. Blanks indicate no data, zero, or below limit of detection. P = modeled prediction from analysis of data on biomarkers A through N; subscripts on D indicate dose/exposure level.

Dose	BioMk "A"	BioMk "B"	BioMk "C"	...	BioMk "N"	Response (Animals)	Response (Humans)	P = Model (Humans)
0.0	■		■	...				P{0.0}
D _{Ambient}	■		■	...			Risk _{Cohort}	≤
D ₁	■		■	...				P{D ₁ }
D ₂	■	■	■	...				P{D ₂ }
D ₃	■	■		...				P{D ₃ }
D ₄	■	■		...				P{D ₄ }
D ₅	■	■		...		■		P{D ₅ }
D ₆	■	■		...				P{D ₆ }
D ₇	■	■		...	■			...
D ₈	■	■		...	■	■		...
D _{High}	■	■		...	■		Risk _{High}	≤

CONCLUSIONS

It should be apparent that the four examples of how the ORNL toolbox can be used are only a limited picture of the applications possible. We believe that the general concept of relative potency or to use the EPA term, toxic equivalent factor, can be used in even more diverse settings than we have presented. In addition to the biological endpoints discussed as examples in this manuscript, the concept may be used in evaluating the potential effects of chemical agents on cardiovascular disease, on neurotoxicity, on reproductive toxicity, and the list goes on.

Of particular importance to the DoD may be the potential for this general concept to be used in the evaluation of mixtures of materials and new materials. Because it is possible to develop a small battery of *in vitro* bioassays to evaluate relative potencies, mixtures and new materials may be screened relatively easily.

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RESTORATION OF DRINKING WATER PIPING WITH NONTOXIC EPOXY LININGS

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ABSTRACT

It is now possible to rehabilitate deteriorated drinking water systems by installing a non-toxic lining which prevents corrosion and leaching of lead and other heavy metals into drinking water. This method is (1) rapid (less than 48 hours), (2) suitable for use aboard ship, inside buildings and underground, (3) effective in bent pipes and pipes of different diameters, (4) economical compared with the cost of replacing pipe, (5) practical for pipe diameters between 1/8" and 24", (6) useful in pipe runs of 1000 feet, (7) suitable for drinking water, waste water, fuel, and other fluids, and (8) minimally disruptive of tenants and their activities. It is recommended for fast, economical, in-place rehabilitation of drinking water systems at Defense facilities around the world.

INTRODUCTION

Corrosion of water mains introduces impurities into drinking water. When these impurities are heavy metals such as lead, the quality of the water may fail to comply with the requirements of the Safe Drinking Water Act and other regulations. The usual remedies for this situation are to replace the piping or to bring in bottled drinking water; several Navy facilities have actually been taken out of service when their drinking water did not measure up to federal standards. This talk will describe another solution - lining the interior of the pipe with a nontoxic coating which keeps impurities out of drinking water.

A chemically-resistant nontoxic epoxy lining for water pipes has been developed at the Naval Research Laboratory. This lining is applied to the interior of pipes by compressed air. The operation causes minimum disruption to tenants or their activities and may be used on systems with multiple bends and varying diameters of pipe. Piping may be lined without removal or disassembly and returned to service within 24 hours. The Navy intends to use this

technology for fast, economical rehabilitation of drinking water systems aboard ship and at shore facilities around the world.

BACKGROUND

This lining was originally developed to solve corrosion problems aboard aircraft carriers. These ships experience severe erosion and corrosion of piping in their waste collection systems, known as collection, holding and transfer (CHT) systems. The Naval Sea Systems Command Detachment responsible for planning and engineering for repairs and alterations of carriers (PERA-CV, Bremerton, Washington) proposed that these piping systems be lined with epoxy linings as part of their Carrier Life- Enhancing Repair Program. As a test, a 20-foot section of CHT pipe aboard the USS MIDWAY (CV 41) was lined in Japan in mid-1986.

Following this favorable test, PERA-CV tasked NRL to test commercial bisphenol epoxy coatings for properties which are significant for CHT piping system linings. The tests were selected jointly by PERA-CV and NRL. None of the commercial coatings was found to be suitable for aircraft carrier CHT systems.¹ Common problems were short pot life, air entrainment during application, and poor adhesion to the copper-nickel alloy pipe. All of the commercial coatings contained solvent; solvents never leave a paint film completely and are always a risk for contamination of water.

PERA-CV then tasked NRL to develop suitable Navy reference formulations for lining 90/10 and 70/30 copper--nickel pipes in both CHT and potable water systems. These coatings have several unique requirements. They must be at least as good as the 1987 standard, a commercially-available Devoe 143 coating (which hardened too fast for convenient use), and they must be formulated from materials approved for use with drinking water so that the same coating may be used in potable water and CHT pipes. They must also be suitable for application by commercial pipe lining methods which rely only on a pressurized gas to propel the paint through the pipe being coated.

We have developed a series of two-component epoxy linings, now known as the "NRL Series 4" linings. The formulations were deliberately kept as simple as possible. The first component contains a liquid epoxy resin, red iron oxide as a colorant, and hydrophobic fumed silica to give body and resistance to flow. The second component, a curing agent, varies in each of the "Series 4" linings.

The coatings were tested in the laboratory for resistance to a wide range of materials found in sewage systems before being approved for a shipboard trial. Initial lab tests sometimes produced films with air bubbles. These provide paths for oxygen, sulfides, and other reactive species to reach the copper-nickel pipe and corrode it, and could not be tolerated. Additives to eliminate entrapment of air were studied and three materials were identified which prevent the formation of bubbles. However, changes in the lining application process were implemented which successfully eliminated bubbles, making unnecessary any changes to the formulations of the linings.

The program was temporarily delayed when new federal legislation² governing the manufacture of the curing agent used in the NRL 4A coating caused the sole producer to stop selling this product. The regulations did not ban production of the material but required all who made or used it to maintain medical records for 30 years, a requirement deemed to be unreasonably costly. Thus it was necessary to reformulate and retest the lining for drinking water applications. Replacement curing agents were identified and tested, using procedures identical to those used in the development of the original lining. All chemical resistance properties and physical characteristics of the original coating were retained in the reformulated product. Linings found acceptable in the laboratory were tested in the field using the same equipment and procedures. A replacement lining, known as NRL 4B, was quickly developed and proven. We have applied for a patent on this coating, and inquiries regarding licensing have been received from commercial applicators.

The process used to line shipboard sanitary piping systems was worked out in detail by the American Pipelining Corporation (San Diego, CA),³ PERA-CV, and NRL. In the past 8 years, sanitary piping systems aboard 12 carriers have been lined. Figure 1 shows an elbow of 6-inch diameter copper--nickel piping from the USS AMERICA (CV 66) which was lined in November 1988 and removed after two years of service. Note that the coating is thicker at the bottom than at other places in the pipe; this is not a disadvantage since almost all corrosion occurs there and the added protection of a thick lining is valuable.

This process is now used routinely on aircraft carriers. The lining has now been installed in all active (and many now decommissioned) carriers and is specified for installation in all new aircraft carriers during construction. In November 1995 the USS JOHN C STENNIS (CVN 74) was the first carrier delivered with the lining already installed. At present two private firms in the United States install this lining.³

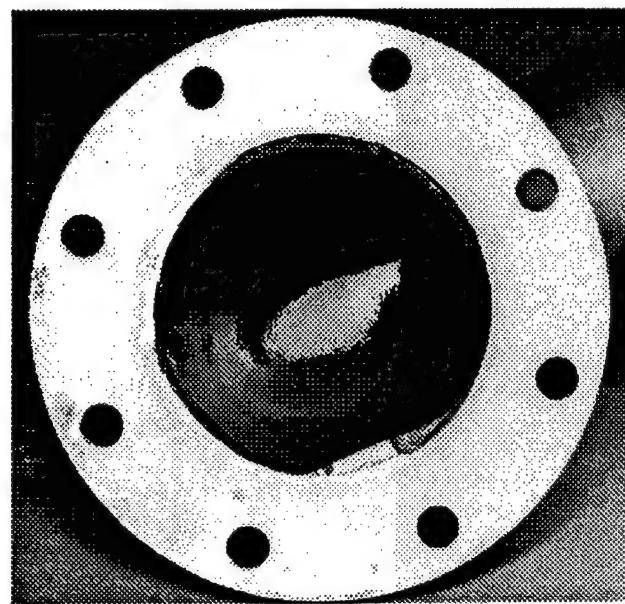


Figure 1. A pipe elbow from the USS AMERICA (CV 66) lined with the nontoxic epoxy lining. Note the increased thickness on the bottom.

LININGS FOR DRINKING WATER PIPES

The technology used aboard aircraft carriers is directly transferrable to piping systems at shore establishments. It comprises the same nontoxic lining and the same process to install

it. The chemically-resistant nontoxic epoxy lining for water pipes is known as NRL 4C, and differs from 4A and 4B only in the curing agent used. The lining contains no solvents, dries in 20 minutes, and resists severe mechanical abuse. The lining releases no color, taste, odor or leachable material into the water.

Materials in contact with drinking water must be tested and approved by the National Sanitation Foundation (Ann Arbor, Michigan) for compliance to NSF Standard 61⁴. NSF, a not-for-profit organization, is the only firm authorized by the Environmental Protection Agency to test and approve materials for contact with drinking water. The testing is in three parts: A review of the properties and history of the ingredients of the lining; application of the lining to pipe, extended contact with water, and tests of the water to ensure nothing has been extracted into it; and examination and certification of manufacturing facilities to ensure that the lining is not contaminated with extraneous material. Because of the requirement that manufacturing facilities must be approved, only manufacturers can obtain NSF certification. To make certification more rapid and less expensive for manufacturers, NRL funded the first two phases of the certification procedure. American Pipelining Corporation has now obtained NSF certification for the NRL 4C lining for use in hot and cold drinking water systems.

The application procedure involves three steps: inspection and necessary repairs before lining; surface preparation by abrasive grit propelled by compressed air; and application of the lining. The technique does not completely eliminate the need to replace deteriorated piping. At the outset of a job pipe thickness is measured with ultrasonic techniques. Pipe with more than 50 percent of its original wall thickness can be lined, but pipe thinner than this must be replaced before lining begins. Pressure in the pipes can reach 60 psi and, although this is not usually considered high pressure, precautions must be taken against rupture of the pipe. Usually only a small amount of pipe is replaced. Lead-based fittings and old solder are removed to the extent possible. Mechanical (flange) joints are installed in the system where it may be necessary to open the system in the future; this is intended to eliminate any future need to cut the pipe and damage the coating.

This technology has been shown to be a proven inexpensive alternative to replacement of pipe, and the Navy now intends to extend this technology to fast, economical rehabilitation of drinking water systems aboard ships and at shore facilities around the world. Pipes are lined without removal or disassembly. Trailer-size air compressors are placed outside the building and air hoses lead inside where they are connected to the piping system. A hose on the other end of the pipe leads outside to a dust collector. Hot dry air is blown through the pipe, and grit is added to remove rust and other contaminants and give the inside of the pipe a rough surface. A 50-micrometers (2 mil, 0.002 inch) profile is required, and is monitored at the front and back of the pipe by making an impression of the profile with replica tape and measuring the profile on the tape with a micrometer. Immediately after cleaning freshly-mixed paint is blown through the pipe, where it hardens in about 20 minutes. Two to three coats are applied in opposite directions to ensure that pinholes and "shadow" areas where the pipe changes diameters are completely covered. The final paint thickness is 300 ± 75 micrometers (12 \pm 3 mils). The stream of hot air is maintained for about 12 hours to dry the paint thoroughly. Pipes are reassembled, flushed with water to remove any contaminants, and pressure tested before the water system is placed back in service. The pipe can be returned to service within 48 hours.

The operation is fast and causes minimum disruption to buildings or their occupants. It is suitable for pipe inside ships and buildings or underground, and is economical compared with the cost of replacing pipe. It may be used on pipe runs as long as 1000 feet, even if they have numerous bends and varying diameters. Temporary water distribution networks are usually installed so that routine activities may continue without disruption.

This method has several disadvantages. No welding or other hot work can be performed on the lined pipe, but soldering is acceptable. The lining is hard and tough, but can be damaged or removed by deliberate and prolonged mechanical abuse. Hot water in the pipes is limited to 160 °F but, because domestic hot water is usually regulated at 140 °F to minimize the danger of scalding, this has not presented a problem. If the pipe is cut, loose paint at the site must be removed before the system is closed.

Plans have been made to demonstrate this technology by lining the drinking water systems in four Navy buildings on the Washington Navy Yard or the Anacostia Naval Annex in Washington, DC during the summer of 1966. Specifications and quality control parameters are available for the NRL 4C lining, and installation and inspection standards are available for the installation process. One outcome of the demonstration project will be the production and distribution of technical and procurement guidance for use by any Defense activity which desires to clean and line its drinking water distribution systems. Using these documents, all future installations of pipe linings in Defense facilities may be carried out according to proven standard procedures.

TABLE 1. SITES SELECTED FOR THE DEMONSTRATION PROJECT

1. ANA2-87 An old house with an addition, now used as a detention facility. The building contains a bath area with toilets, showers, and sinks at one end of the building, and two cells with toilets and sinks at the far end.
2. ANA93 A 2-story Bachelor Officers' Quarters with 30 sleeping rooms. This is similar to a commercial motel; each room has a shower, toilet and sink.
3. ANA171 The "Legends" snack bar, formerly the "Acey-Deucey" NCO club. The building has a kitchen area with sinks and two sets of men's and women's restrooms at opposite ends of the building.
4. WNY220 A four-story mixed use industrial/warehouse/office, originally constructed for use as a warehouse. Men's and women's toilets on each floor are stacked and connected by vertical supply lines.

At the conclusion of this work, the technology will be transferred to the Naval Facilities Engineering Command (NAVFAC), the Air force Office of Installations and Logistics, the Army Corps of Engineers, and their field activities. We will prepare a Guide Specification for Drinking Water Pipe Linings. NAVFAC routinely uses guide specifications for construction and repair activities of all kinds. This document will be indexed, reproduced, and distributed to engineering field activities in the same manner as current guide specifications. We will provide on-site assistance if requested for the first few installations of the coating, and will incorporate

lessons learned into the guide specification. We will be available for consultation and advice after the document is issued and, if funding is available, will update the document as circumstances require.

The guide specification will contain at least the following information: applicable federal health and safety laws and regulations; indications where use of the coating, or replacement of pipe is recommended; formulation and quality control limits for the lining; safety precautions to be followed during installation; procedures for pipe cleaning, surface preparation, lining application and curing; and procedures for testing and inspecting installed linings.

CONCLUSIONS

Epoxy coatings have been formulated and all necessary certifications for contact with drinking water have been obtained. The lining will be installed in three DoD buildings this summer. Technical and procurement guidance will be made available to all DoD activities who wish to use this technology to rehabilitate drinking water systems. The technology is also applicable to waste water, fuel, and other piping systems.

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NATURAL ATTENUATION OF EXPLOSIVES IN GROUNDWATER AT ARMY SITES

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Abstract

Cleanup of groundwater contaminated with explosives can be prohibitively expensive. Achieving regulatory limits when concentrations reach low levels is often especially difficult. Natural attenuation may be an attractive alternative to available remediation technologies at sites that meet well-defined selection criteria, acceptable risk levels, and that satisfy specific regulatory concerns. The objectives of this project are to demonstrate that attenuation of explosives can be established through appropriate site monitoring, to develop guidance for selection of natural attenuation as a remediation alternative, and to develop a protocol for establishing a site monitoring plan and point(s) of compliance. The protocol for implementation of natural attenuation will be developed from data gathered from at least one site exhibiting explosives contaminated groundwater. An initial data gathering step will include a synthesis of what is known concerning degradation processes, contaminant transport and site geology/hydrology. Existing data will be supplemented by appropriate field investigations. The final protocol will describe selection criteria and considerations, an approach to site characterization and monitoring, parameters to assay and analytical methods, and establishment of points of compliance.

INTRODUCTION

Research has demonstrated that certain explosives are naturally immobilized in soil systems under specific environmental conditions¹. Explosives are also degraded by microbial and/or abiotic processes^{2, 3, 4}. Any of these sets of processes may provide evidence of attenuation in the subsurface. Furthermore, the hydrologic and geologic dynamics of the site groundwater together with the location and risk associated with potential contaminant receptors may also provide support for selecting natural attenuation as a remediation alternative. If the site is isolated making receptors far removed, and/or if the groundwater flow is extremely slow, risk to receptors may be deemed acceptable.

Natural attenuation is not a "no action" remediation alternative. Selection of natural attenuation requires a thorough understanding of relevant site hydrology, geology, and the contaminant plume. Natural attenuation also requires long-term site monitoring to assure that receptors are being protected and that no detrimental changes in projected contaminant migration toward receptors have occurred. The objectives of this study are to provide guidance to site personnel for selection of natural attenuation as a remediation alternative, for monitoring the site for prolonged protection and regulatory compliance, and for eventual site closure.

Natural attenuation has been defined as "the reduction of contaminant concentration to environmentally benign levels through natural processes"⁵. Active processes include, but are not limited to, advection, dispersion, diffusion, volatilization, biotic degradation (mineralization and transformation), sorption/desorption, ion

exchange, complexation, abiotic transformation, and plant and animal uptake. This definition excludes any intervention to enhance natural processes.

Studies of natural attenuation for petroleum hydrocarbons by the Air Force in cooperation with EPA have contributed significantly to maturation of the technology^{6, 7, 8, 9, 10, 11, 12, 13}. Natural attenuation of BTEX has also been investigated at several sites: Sleeping Bear Dunes, MI^{14, 15}, Sampson County, NC¹⁵, Rocky Point, NC¹⁵. At least three states have developed guidelines for permitting natural attenuation, Wisconsin^{16, 17, 18}, Florida^{19, 20} and Michigan²¹.

TECHNICAL DESCRIPTION

Site Selection and Characterization

An ideal candidate site for demonstrating natural attenuation is one in which the groundwater has (1) sufficient residence time to allow natural attenuation processes to occur, (2) limited or no risk of contamination of local receptors, e.g. drinking water wells, streams, wetlands, and (3) a receptive local/regional regulatory community. We selected the Louisiana Army Ammunition Plant at Bossier City, Louisiana as our initial demonstration site for these and several other reasons. The source of contamination, several liquid waste storage lagoons, was removed six years ago. Absence of an active source of contamination will simplify the interpretation of the groundwater data and the plume migration. The site has been extensively characterized in terms of geology, hydrology and contamination in soils and groundwater. The area of interest already has over 50 groundwater monitoring wells; therefore, cost for installation of wells will be minimal. Contaminant data for many of these wells is available for each year since remediation of the lagoons. Region VI of the EPA has been receptive to considering natural attenuation as a remediation alternative for the site.

Although this demonstration site has received extensive characterization, we hope to develop procedures for site characterization that will minimize the cost of implementing site characterization for future users. We anticipate a need for good geology, hydrology and contaminant data that focus on the objectives of natural attenuation. An objective of the study is to define an efficient, cost-effective sampling protocol.

To justify selection of natural attenuation, the site must be sufficiently characterized to support the following performance criterion: The rate of contaminant immobilization/degradation is sufficient to protect the nearest possible receptor over a "reasonable" period of time. The definition of "reasonable" will usually be in terms of local risk assessments and regulatory concerns.

Monitoring

A site monitoring plan consisting of monthly sampling of 30 existing wells has been initiated. Monthly sampling will occur for the first six months of the project only. After that, sampling will occur quarterly for the remainder of a two year period. The monthly sampling will allow us to refine sampling protocols, identify sources of variability and determine the degree of variability in the site. Parameters that will be monitored initially include the following: explosives and their transformation products, potential electron acceptors (iron, manganese, sulfate, nitrate/nitrite), dissolved oxygen, conductivity, pH, total dissolved solids, and water level.

Modeling

A three-dimensional, multi component transport code is under development to describe and predict the subsurface fate of explosives. While code preparation is being conducted on a Unix workstation platform; eventual migration to other platforms (personal computers to multi processor systems) is anticipated. Long-range plans include bringing a mature version of this code into the DoD Groundwater Modeling System (GMS), a standard user interface with which to visualize simulation input/output. Available GMS tools will be used to visualize hydrogeology, monitoring well data, and model predictions.

Guidance Document

A user-friendly guidance document will be prepared for use by facilities personnel and others who must consider natural attenuation as a remediation alternative. The document will include pertinent site characterization guidance, monitoring protocols, selection of compliance criteria, and guidance on site closure.

CONCLUSIONS

Natural attenuation of explosives will be demonstrated at Louisiana Army Ammunition Plant in order to develop guidance on selection and implementation of natural attenuation as a remediation alternative. The demonstration will proceed through a comprehensive groundwater monitoring plan, adoption of a groundwater model and preparation of an implementation protocol.

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IN SITU DECHLORINATION OF SOLVENTS IN SATURATED SOILS

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ABSTRACT

Use of chlorinated solvents has led to extensive soil and groundwater contamination. Current aerobic treatment methods, such as pump-and-treat with carbon sorption or air stripping, are limited and often cost-prohibitive. Researchers have isolated microbial cultures capable of reductively dechlorinating tetrachloroethene (PCE) to ethene (ETH). Field studies have shown reductive dechlorination of chlorinated solvents to be stimulated by the addition of electron donors. Based on these results, this project utilizes indigenous bacteria and added electron donors for degradation of PCE in the field. The approach is designed to achieve a rigorous mass balance on electron donors, electron acceptors, and microbial carbon/energy sources. The effort is aimed at validating reductive dechlorination in a realistic field situation.

1.0 INTRODUCTION

PCE and trichloroethene (TCE), have been used widely since the 1940s. This use, in addition to improper handling and storage, has led to extensive groundwater contamination at both industry and military sites. The U. S. Air Force is responsible for an estimated 1700 chlorinated solvent-contaminated sites which will require some form of cleanup.

Current chlorinated solvent remediation technologies are costly, ineffective, and/or impractical. The use of pump-and-treat technology alone for remediating chlorinated solvent-contaminated aquifers is often unrealistic. Carbon sorption and air stripping are the methods currently used with pump-and-treat. Carbon sorption is a costly nondestructive method. Air stripping merely transfers the contaminant from the water phase to the air phase. In some instances, the contaminated air stream is regulated and requires

treatment. Some chlorinated solvents have been shown to be cometabolically biodegraded *in situ* under aerobic conditions, via methane-oxidizing (1) or phenol-oxidizing (2, 3) microorganisms. However, the successful application of cometabolic aerobic bioremediation may be limited due to competitive inhibition between the cosubstrate and the chlorinated solvent, intermediate product toxicity via chlorinated solvent oxidation, the difficulty of adding poorly soluble cosubstrates such as methane and oxygen to the groundwater, and the relatively high cost of maintaining aerobic conditions *in situ*.

Chloroethenes can be reductively dechlorinated (4-9). Development of a cost-effective *in situ* anaerobic biotreatment technology for groundwater contaminated with chlorinated solvents is urgently needed by the DOD and industry. A microbial culture capable of reductively dechlorinating PCE to ETH with efficient use of electron donors has been isolated at Cornell University (5). In the field, studies with site materials and isolated test plots have shown reductive dechlorination of chlorinated solvents to be stimulated by the addition of electron donors (10-12). Based on these results, this field effort utilizes indigenous bacteria and added electron donors to stimulate the degradation of PCE to ETH in the subsurface at Naval Air Station Fallon, NV (NASF). The study is being conducted through a partnership between the U. S. Air Force Armstrong Laboratory Environics Directorate (AL/EQ), the U. S. Navy, the U. S. Environmental Protection Agency National Risk Management Research Laboratory (NRMRL), Cornell University, and Battelle Memorial Institute.

The objective of this research is to extend positive laboratory results to an *in situ* field demonstration of PCE dechlorination. The field system allows researchers to investigate the addition of various electron donors to enhance the reductive dechlorination already occurring at the site, in addition to investigating dechlorination through natural attenuation and iron electrodes. The field investigation consists of five semi-enclosed treatment lanes, with two outside lanes used for natural attenuation and the iron electrodes. A hydraulic gradient will be applied to all five lanes. Using controls, this approach is designed to achieve a rigorous mass balance on the electron donors, electron acceptors, and microbial carbon/energy sources. A detailed understanding of the dechlorination process will lead to more efficient, cost-effective, and reliable strategies for the bioremediation of PCE and related compounds.

2.0 BACKGROUND

2.1 REDUCTIVE DECHLORINATION OF CHLOROETHENES IN THE LABORATORY

Cornell University was the first to report complete dechlorination of PCE to ETH, a process of sequential reduction steps with TCE, dichloroethene (DCE), and vinyl chloride (VC) as intermediates (13):



In contrast to hydrocarbons which can be directly biodegraded, reductive dechlorination of chloroethenes requires the addition of electron donors (5). The original focus of the Cornell studies used methanol (MeOH) and developed a culture capable of rapidly dechlorinating high concentrations of PCE to ETH. However, further research revealed that H₂, not MeOH, is the direct electron donor responsible for PCE dechlorination (6). MeOH and other reductants found to support dechlorination merely serve as H₂ precursors.

Electron donors other than MeOH offer several benefits for reductive dechlorination of chloroethenes. Substrates, such as butyrate, lactate, and ethanol-benzoate, are not direct methanogenic substrates. They eliminate competition for the supplied donor itself, as they (unlike MeOH) are not methanogenic. H₂ is a direct fermentation product of these substrates. It is produced slowly at low levels providing for complete

mineralization of PCE, thus favoring dechlorination over competition for the substrates (13). These results suggest that strategies utilizing slow, steady H₂ delivery are best to stimulate and maintain reductive dechlorination.

Gossett and Zinder have evaluated the acclimation, induction, and kinetics of the processes catalyzed by their enrichment to obtain a better understanding of the culture mechanisms. A novel bacterium appears to be solely responsible for the PCE dechlorination. A vitamin solution containing vitamin B₁₂ sustains the dechlorination, while fermented yeast extract and sewage sludge supernatant are promising nutrient sources. Insight from these microbial and nutritional studies provides useful information when attempting to harness the reductive dechlorinating capabilities of indigenous bacteria located in PCE-contaminated groundwater.

2.2 PREVIOUS FIELD STUDIES FOR *IN SITU* REDUCTIVE DECHLORINATION

At the DuPont Victoria Plant in Victoria, TX, a test zone in a PCE-contaminated aquifer underlying a former landfill was selected for evaluation. Microbial reductive dechlorination was stimulated by pumping the electron donor benzoate or a sulfate solution into a recirculating groundwater treatment system. After two years of anaerobic treatment, PCE and lesser-chlorinated ethenes were reductively dechlorinated *in situ* to below detection limits (11).

In another study, microcosm studies were conducted with PCE-contaminated core materials collected from the Coast Guard Air Station in Traverse City, MI. Four fatty acids and three alcohols were tested for their ability to act as sources for reducing equivalents for PCE dechlorination (10). Dehalogenation activity was observed as a result of electron donor addition within one week with some amendments while others required two weeks or more. This study indicated that the availability of electron donors is essential for reductive dechlorination of PCE and TCE in the environment (10).

Information gained from these studies and others show the potential for cleanup technologies aimed at stimulating reductive dechlorination of chlorinated ethenes in environments where there is low availability of carbon and energy sources. Results of these studies, in conjunction with the laboratory work performed at Cornell University, are being applied in the field at NASF.

2.3 NASF SOIL MICROCOISM STUDIES

In the laboratory, several electron donors have been demonstrated to stimulate anaerobic fermentation, H₂ production, and reductive dechlorination of PCE using NASF soils (Gossett, 1996). Anaerobic fermentation products and PCE dechlorination capacity of five electron donors [lactate, butyrate, propionate, ethanol (EtOH), and benzoate] and three electron donor mixtures using benzoate plus EtOH have been compared. PCE dechlorination to TCE was observed in the lactate-fed bottles after 150 days of incubation. Low levels of TCE were also detected in butyrate- and benzoate-fed bottles. The addition of nutrients (yeast extract and/or vitamins) appeared to contribute to more rapid PCE dechlorination, as indicated by comparing the rate of PCE removal and TCE production in lactate-fed bottles.

Sulfate reduction in the NASF soil microcosms suppressed H₂ accumulation, methane production, and PCE dechlorination, though the PCE results are inconclusive. More positive results of PCE dechlorination during sulfate reduction were obtained from work done by the EPA NRMRL (Gossett, 1996). The rate of electron donor consumption in the Cornell studies decreased in the following order:

EtOH >> lactate > butyrate and propionate >> benzoate.

EtOH was fermented to a mixture of acetate and propionate, suggesting that EtOH served as both a fast source of H₂ and a slower source of H₂ via propionate production and the subsequent fermentation of propionate to acetate and H₂. If H₂ is the primary electron donor for PCE dechlorination in the NASF microcosms, the Cornell studies suggest that slow release of H₂ is apt to provide the best condition for suppressing methanogenic competition with PCE dehalogenators and enhancing PCE dechlorination (Gossett, 1996).

3.0 FIELD STUDY, NASF

Site 1 at NASF was selected for enhancement of dechlorination by indigenous microbes through the addition of various electron donors. The field system is designed to enhance the reductive dechlorination already occurring at the site. Natural attenuation will serve as the control while reductive dechlorination through the use of an iron electrode will be field-evaluated.

3.1 SITE GEOLOGY

NASF is located 60 miles east of Reno, NV and was established as a military facility in 1942 as part of the Western Defense Program. The Crash Crew Training Area (Site 1) consists of an unlined, earth-bermed burn pit, previously associated with two above ground fuel storage tanks (Figure 1). From the mid-1950s to April 1988, the burn pit was used to conduct fire training for NASF personnel. The pit was reportedly used to burn an estimated 1.1 million gallons of flammable liquids, fuel farms waste products, napalm, lubricants, and solvents. An estimated 99% of the material burned was fuel and lubricants.

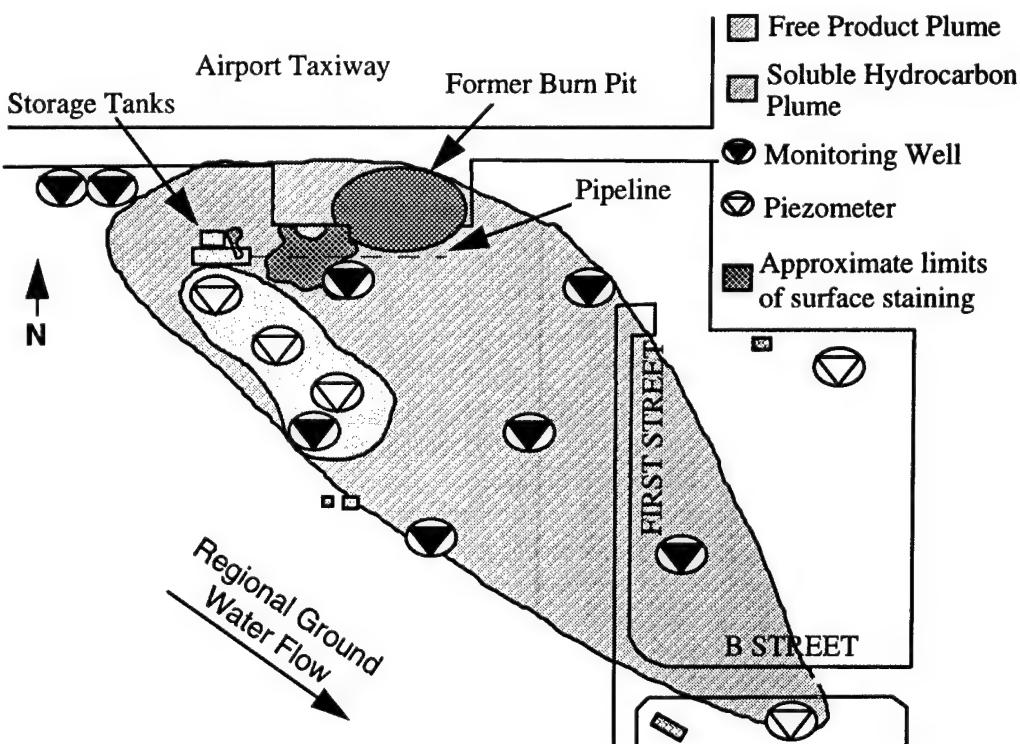


Figure 1. Site area map of Site 1, NAS Fallon, NV.

Sandy soils cover the site at NASF and extends to a depth of approximately 4 ft. Beneath the sandy surface cover is a layer of clay-rich silts and sands, approximately 2 ft thick and appearing to be laterally

continuous across the site. The fine-grained layer and sand layer form an unconfined aquifer which is laterally continuous across the site. At the bottom of the unconfined aquifer is a sandy silt and clay layer which has a thickness in excess of 5 ft. The clay layer is nearly 20 ft thick across most of the site (14).

The water table surface in the Fallon area experiences seasonal and daily fluctuations due to irrigation and rainfall influences. Groundwater at the site is perched on a regional lake bed clay layer at a depth of 8 to 10 ft. The regional clay layer acts to impede contaminant movement from the local aquifer to deeper aquifers. The groundwater flow direction is to the south in the northern half of the site and to the southeast in the southern half of the site. The average hydraulic gradient is 4.0×10^{-4} ft/ft (14).

3.2 SITE CONTAMINATION AND GENERAL GROUNDWATER CHEMISTRY

Primary contaminants reported at Site 1 include chlorinated solvents, JP-5, gasoline, and waste oil. Most chlorinated solvent contamination at Site 1 is associated with free product on the water table with lower concentrations in the groundwater. The dissolved-phase plume at Site 1 contains both fuel and chloroethene related constituents (Table 1). Maximum concentrations for all constituents were found immediately adjacent to the burn pit, approximately 50 m from the test site (Figure 1). The maximum PCE and TCE concentrations reported were 680 and 340 $\mu\text{g}/\text{L}$ (14), respectively. 1,2-cis-DCE is a known metabolite of TCE dechlorination, and its presence suggests biological reductive dechlorination of PCE at Site 1.

TABLE 1. CONTAMINANT CONCENTRATION AND GENERAL GROUNDWATER CHEMISTRY

Contaminant	Concentration ($\mu\text{g}/\text{L}$)	General Water Chemistry	Concentration
PCE	2.6 - 680	pH	7.60 - 9.11
TCE	9.9 - 340	Conductivity	48,900 - 3,750 μmhos
1,1-DCE	1.5 - 8.0	Total Alkalinity	569 - 701 mg/L
t-DCE	1.0 - 101	O-P	0.74 - 3.08 mg/L
c-DCE	1.5 - 609	Cl ⁻	661 - 15,100 mg/L
VC	1.1 - 2.9	SO ₄ ⁻²	386 - 8,650 mg/L
toluene	1.3 - 18	NO ₂ (N)	< 0.20 mg/L
benzene	1.2 - 242	NO ₃ (N)	< 2.68 mg/L
ethylbenzene	2.0 - 152	NH ₃ (N)	< 0.23 mg/L
xylenes	1.2 - 450		

3.3 FIELD TEST TREATMENT SCENARIO

This field study involves the use of five semi-enclosed treatment lanes separated by four high-density polyethylene (HDPE) sheetpiles. Each lane represents a unique treatment scenario using different electron donors and nutrient additions. An artificial hydraulic gradient is being imposed in each lane and controlled via groundwater pumping from influent injection and effluent extraction wells. Each treatment lane is scheduled to receive different nutrient and electron donor additions (Table 2). Two of the three inside lanes will receive organic electron donors (lactate or EtOH plus benzoate) and nutrients (vitamins plus yeast extract). The third inside lane will receive high yeast extract concentrations plus vitamins, with yeast extract acting as the electron donor. One of the outside lanes will be a control lane operated without adding electron donors, vitamins, or yeast extract to monitor nonbiological losses and losses due to intrinsic PCE biotransformation. The second outside lane will not be fed an electron donor, vitamins, or yeast extract. An iron electrode will be installed *in situ*, downstream of the injection well, to produce H₂ via iron oxidation and the reduction of H⁺ ions in water to H₂.

TABLE 2. FEED SCHEDULE FOR ELECTRON DONORS, VITAMINS, AND YEAST EXTRACT

Lane	Treatment Amendments
A (outside)	Control (natural attenuation)
B (inside)	Ethanol plus benzoate, vitamin solution, and yeast extract
C (inside)	Lactate plus vitamin solution and yeast extract
D (inside)	High yeast extract plus vitamin solution
E (outside)	Electrode potential with iron (no vitamin solution or yeast extract added)

Initial electron donor concentrations are shown in Table 3 and are to be modified as needed. The concentrations are based on the NASF soil microcosm studies performed at Cornell. Over 16 g/L lactate, 8 g/L benzoate, or 8 g/L EtOH would be required to satisfy the total sulfate burden in each lane. Because cost and the potential for clogging the aquifer render such high electron donor concentrations prohibitive, the added electron donors are not expected to satisfy the electron donor-demand for sulfate reduction. Vitamin and yeast extract concentrations are shown in Table 4. The high yeast extract concentration (200 mg/L) is applied to Lane D.

TABLE 3. INFLUENT ELECTRON DONOR CONCENTRATIONS FOR LANES B AND C

Lane	Electron Donor	Electron Donor Concentration (mg/L)
B	Lactate	540
C	Ethanol	140
	Benzoate	170

TABLE 4. INFLUENT AND YEAST EXTRACT CONCENTRATIONS

Vitamin/Yeast Extract	Concentration (mg/L)
d-biotin	0.01
folic acid	0.01
pyridoxine hydrochloride	0.05
thiamin hydrochloride	0.025
riboflavin	0.025
nicotinic acid	0.025
DL-calcium pantothenate	0.025
vitamin B ₁₂	0.025
p-aminobenzoic acid	0.025
lipoic acid	0.025
yeast extract amendment	20
high yeast extract	200

3.4 TREATMENT LANE CONFIGURATION

Figure 2 shows the plan view of the five treatment lanes. The treatment lanes are oriented in the direction of the groundwater flow. Each lane is dependent on one extraction well located upgradient from the treatment area and a cluster of three injection wells at different depths in each lane. The injection and extraction wells are separated by 17.5 ft. Injection and extraction flowrates are established to induce an artificial hydraulic gradient without allowing cross-contamination between lanes. Influent groundwater is pumped into the injection wells at a rate of 60 gallons per day (gpd), split between the three levels at 8 ft, 10 ft, and 12 ft below ground surface (bgs). Effluent groundwater is pumped from the

extraction wells at 200 gpd. The nutrient feed solutions are blended with the influent water immediately upstream of the injection wells.

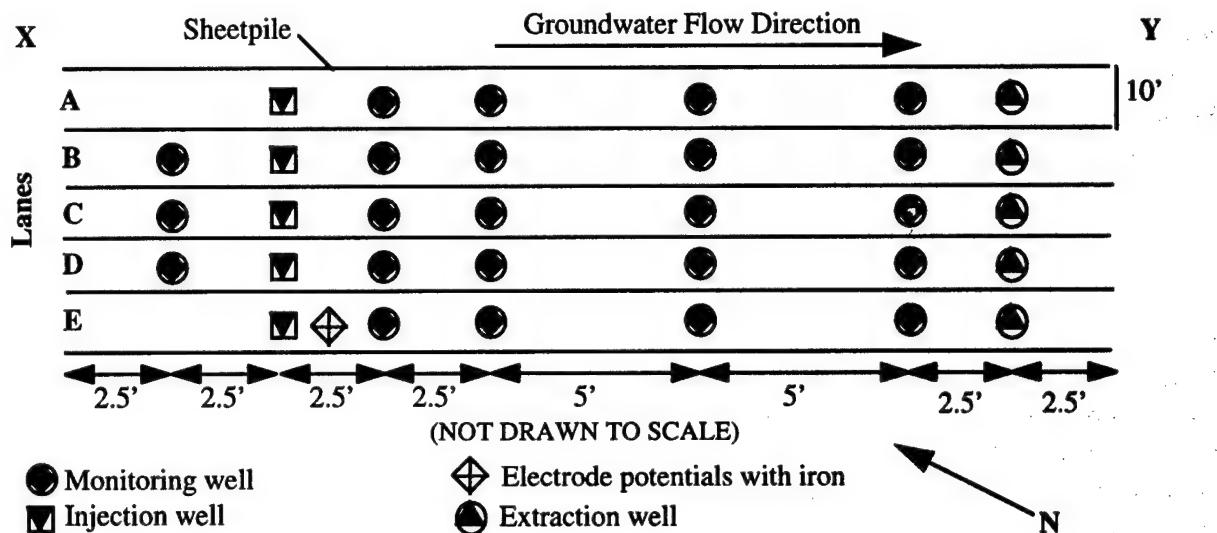


Figure 2. Plan view of the five treatment lanes (Lanes A through E).

A cross section of a typical inside lane is shown in Figure 3. There are four bi-level groundwater monitoring well clusters between each pair of injection and extraction wells, located along the centerline axis of each lane. Each bi-level monitoring well cluster has well screens at 8 ft and 12 ft bgs.

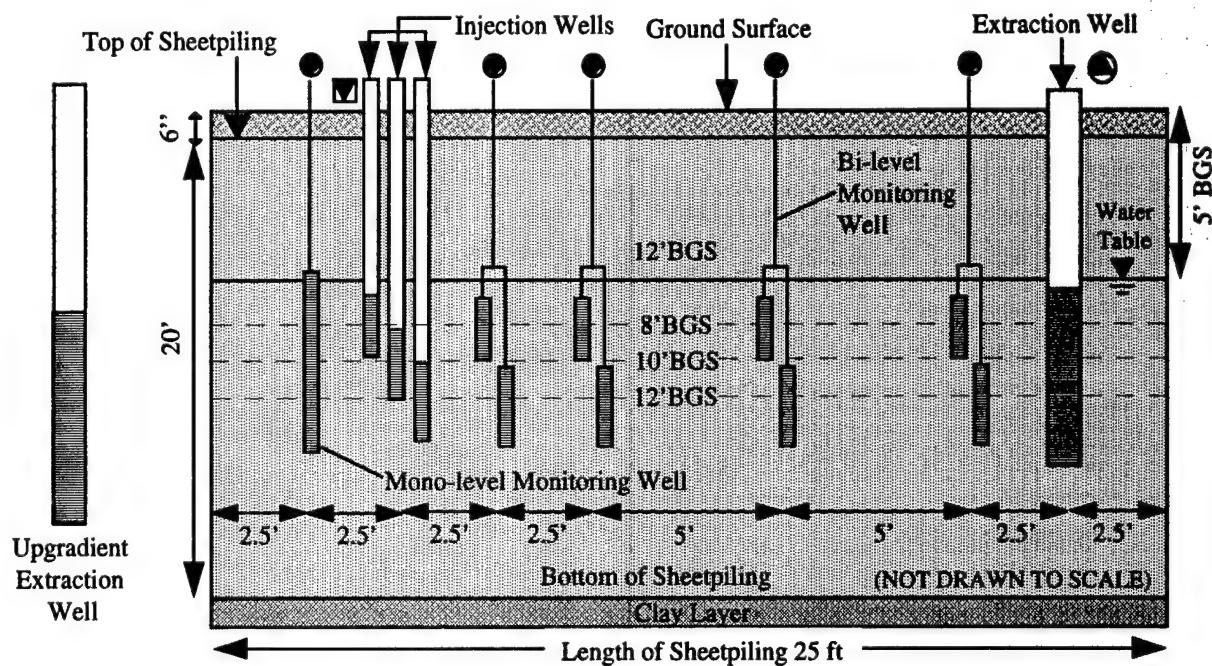


Figure 3. Cross section of a typical inside lane

A cross section of a typical outside lane is shown in Figure 4. There are four mono-level groundwater monitoring well clusters between each pair of injection and extraction wells, located along the centerline

axis of each lane. Monitoring well screens are at 10 ft bgs. Table 5 shows depth and screened intervals for injection and monitoring wells.

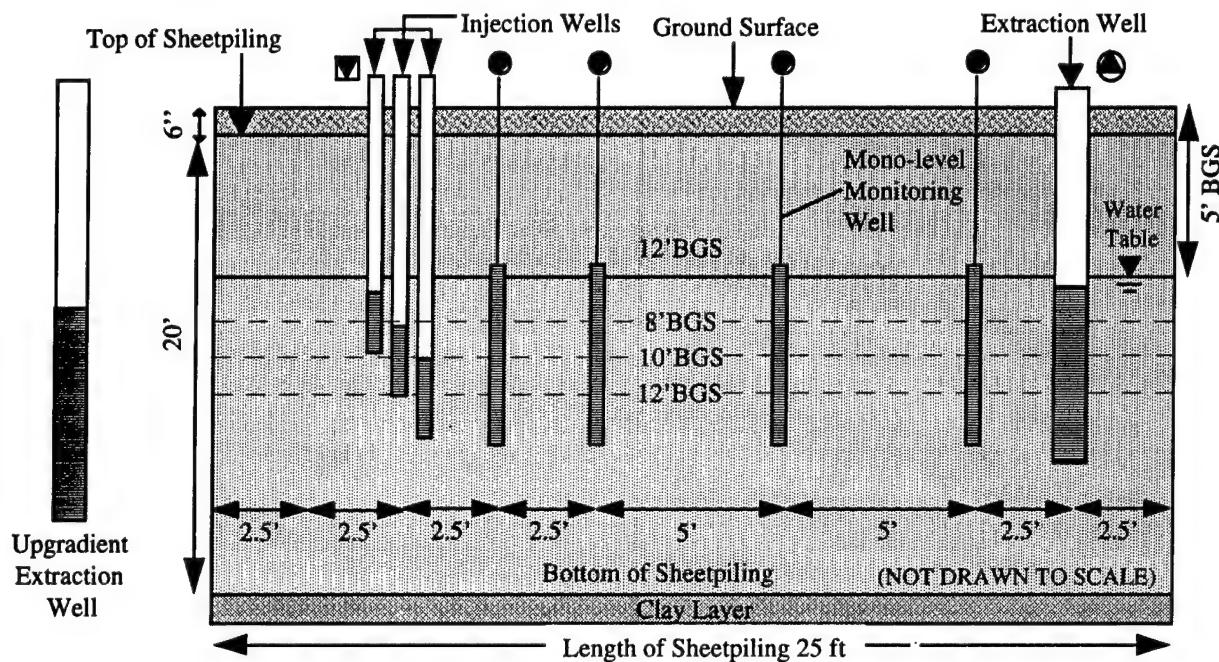


Figure 4. Cross section of a typical outside lane

TABLE 5. WELL DEPTHS AND SCREENED INTERVALS

Lane	Well	Depth (ft)	Screened Interval (ft)
A - E	Tri-level injection wells	8	6 to 8
		10	8 to 10
		12	10 to 12
A - E	Extraction wells	10	5 to 10
A - E	Mono-level monitoring wells	8	6 to 8
B - D	Bi-level monitoring wells	8	6 to 8
		12	10 to 12

Four sheetpiles, installed at a depth of 20 ft, separate the five treatment lanes. The sheetpiles are installed approximately 4 ft into the clay layer which separates the surface aquifer from the deeper, confined aquifer. The sheet piles are 25 ft long, extending 5 ft upstream of the injection wells and 2.5 ft downstream of the extraction wells. Each treatment lane is 10 ft wide.

An iron electrode will be installed in Lane E. The iron acts as an anode, giving off electrons which go toward the reduction of hydrogen ions (H^+) to dissolved H_2 gas. The iron anode is electrically connected to another metal other than iron (i.e., zinc), which acts as the cathode in an *in situ* galvanic cell. H_2 is expected to contribute to the reductive dechlorination of PCE. H_2 which does not contribute to PCE dechlorination will be consumed by lithotrophic bacteria or volatilize to the atmosphere.

3.5 SAMPLING SCHEDULE

The sampling schedule is shown in Table 5. Organic analyses include PCE, dechlorination byproducts (TCE, DCE, and VC), and electron donor concentrations. Dissolved gas analyses include CH₄, H₂S, and CO₂. Inorganic analyses include sulfate, nitrate, iron, DO, pH, alkalinity, and conductivity.

Dissolved gas is scheduled for analysis less frequently than the organic and inorganic analytes. Influent lines and the first two bi-level groundwater monitoring wells will be tested during the first months of the test to determine the extent of anaerobic production of methane and sulfide gasses. Once anaerobic activity is established and confirmed analytically, changes to the dissolved gas monitoring will be evaluated. In addition to the analyses described in Table 5, the following groundwater analyses will be performed for each monitoring well sample point: pH, temperature, conductivity, redox potential, and DO concentration.

TABLE 6. SAMPLING FREQUENCY

Sampling Events	Organic Analyses	Dissolved Gas Analyses	Inorganic Analyses	Field Analyses
First Month	50 per week	10 per week	50 per week	50 per week
Months 2 to 12	50 per month	20 per month	50 per month	50 per month

CONCLUSIONS

To date, data collection has been limited to microcosm studies performed at Cornell. This effort is aimed at validating the technology of enhanced *in situ* reductive dechlorination in a field situation. A detailed understanding of *in situ* dechlorination will lead to more efficient, cost-effective, and reliable strategies for bioremediation of PCE and related compounds. Insight from this study will be useful in modeling the fate of compounds and predicting the success of natural attenuation of chlorinated solvents. Understanding the microbiology will enable researchers to understand and control processes which remove chloroethenes from the environment. The information will directly feed into the development of a protocol to serve in the assessment of successful application of enhanced *in situ* reductive dechlorination.

ACKNOWLEDGMENTS

This field effort marks the transition of 16 years of investment by AL/EQ and Cornell University in the remediation of chlorinated solvents from the laboratory to the field. Through the combined financial, technical, and consultant efforts of the group involved in the effort at NASF a highly successful laboratory program is being realized in the field.

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CONTRIBUTED MANUSCRIPTS

DESTRUCTION OF NITROCELLULOSE USING ALKALINE HYDROLYSIS

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ABSTRACT

Due to demilitarization activities in the United States, large amounts of energetic materials which have been accumulated over the years in various manufacturing and military installations, have to be dealt with in an environmentally acceptable manner. Historically, the method of choice for destruction of energetic materials has been open burning or open detonation which are neither safe nor environmentally desirable. Alkaline hydrolysis appears to be a simple, inexpensive method for breaking explosives and propellants down to non-energetic materials that can be directly disposed or further treated biologically. Nitrocellulose is one of the energetic materials classified as reactive (40 CFR § 261.21) and is listed under the Resource Conservation & Recovery Act (RCRA). This RCRA classification designates energetic materials as a hazardous waste. This study focused on the kinetics of decomposition of nitrocellulose using sodium hydroxide at different dosage levels, temperature, and contact times. Significant levels of denitration and breakdown of the backbone of cellulose structure were achieved by this method. The post-digestion products consist of organic and inorganic substances with sodium nitrite and nitrate being the major nitrogen containing compounds. The ratio of nitrite-N to nitrate-N is slightly changed at different sodium hydroxide concentrations but it approaches a value of 3 regardless of the degree of digestion. The time required for complete destruction varies with concentration of sodium hydroxide and temperature. Kinetic modeling showed that the process follows a pseudo-first-order rate law. The present work indicates that alkaline digestion may be the technology of choice for the destruction of nitrocellulose in various gun and rocket propellants, and for the treatment of nitrocellulose laden effluents from munitions manufacturing facilities.

INTRODUCTION

In demilitarization activities, Environmentally acceptable degradation of associated with energetic material waste to non-energetic forms is a critical objective. Large amounts of energetic materials which have been accumulated over the years in various manufacturing and military installations, have to be dealt with in an environmentally acceptable manner. Historically, the method of choice for destruction of energetic materials has been open burning or open detonation which are neither safe nor environmentally desirable.

Cellulose nitrate, also more commonly called nitrocellulose shown in Figure 1, is one of the important derivatives and has been widely used as wood finish, ink bases, filter membranes and explosives. High nitrogen content Nitrocellulose, a principal energetic ingredient of propellants, has been classified as reactive (40 CFR § 261.21) and is listed under the Resource Conservation & Recovery Act (RCRA). This RCRA classification designates energetic materials as a hazardous waste.

Various physicochemical and biological processes have been developed for the removal of nitrocellulose and nitrocellulose fines in industrial process wastewater. These removal processes classified as a physicochemical mean include microfiltration, coagulation, sedimentation, air floatation, and alkaline or acid hydrolysis.¹⁻⁵ It is also well documented in the literature that nitrocellulose was resistant to direct biodegradation under either aerobic or anaerobic conditions.⁵⁻⁹ Therefore, among the various processes, alkaline hydrolysis appears to be a simple, inexpensive method for breaking nitrocellulose down to non-energetic materials that can be directly disposed or further treated biologically.

Kenyon and Grey¹ reported the presence of a wide variety of organic and inorganic products resulting from the alkaline hydrolysis of nitrocellulose such as nitrates, nitrites ammonia, cyanide, malic, oxalic, glycolic, trioxylglutaric, dioxybutyric, malonic, tartonic and other unidentified complex acid, sugar, modified cellulose and their nitrates, and partially denitrated cellulose nitrate. Edge et al.¹⁰ suggested two possible degradation pathways, shown in the Figure 2, which were based on the formation of nitrites and nitrates by the action of alkali on nitrocellulose. One of these is simple ester hydrolysis where any acid formed would be neutralized by degrading base and hence any degradation nullified. The other possible mechanism could result in the production of carbonyl groups forming an oxidized cellulose.

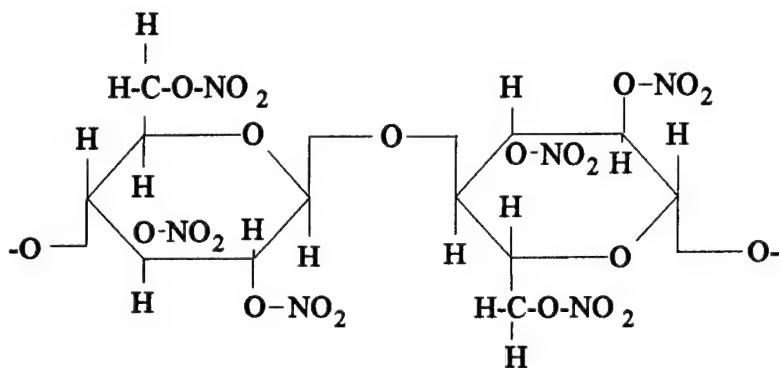


Figure 1: Chemical structure of fully nitrated nitrocellulose

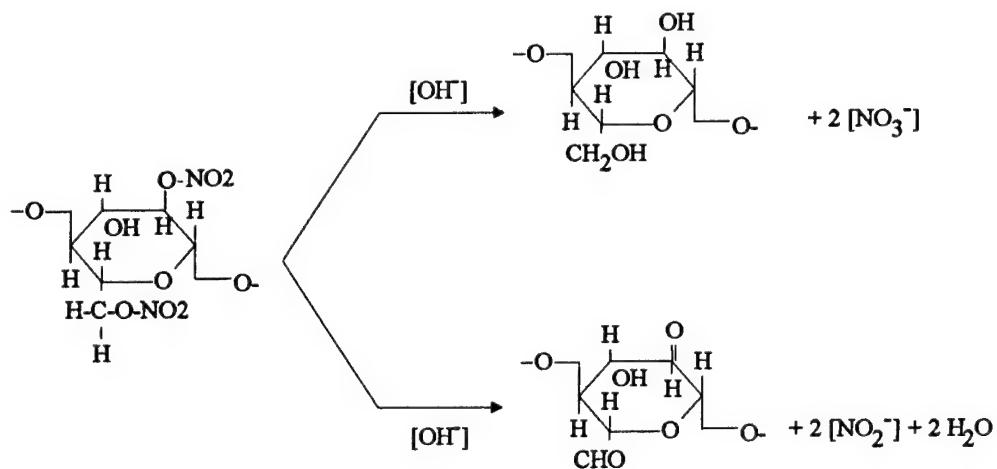


Figure 2: Two Possible Mechanisms of Nitrocellulose Hydrolysis by Alkaline Attack

Quantitative studies of this reaction are more or less fragmentary. The formation of nitrites and nitrates by the action of alkaline hydrolysis of nitrocellulose has been quantitatively measured^{1, 4, 7}. Various authors have also studied in a quantitative manner the effect of certain variables such as the type of bases, concentration of alkaline solution, temperature, and time^{1, 7}.

Unfortunately, there was no extended studies of the kinetics of decomposition of nitrocellulose by alkaline hydrolysis. Therefore, the purpose of this study is to establish the relationship between nitrocellulose and base solution, by the application of simple analytical methods at each step of the degradation process.

As for nitrocellulose hydrolysis, the literature provides inadequate data on kinetics. This may be resulted from lack of a simple and accurate analytical method to measure nitrocellulose directly. With regard to this, the literature reports several methods to determine directly or indirectly unutilized nitrocellulose to ensure nitrocellulose quality in chemical and biological processes^{3, 11}. On the present studies, total suspended solid (TSS), the most common method at the plant, was measured and to assume that all TSS was nitrocellulose. Nitrates and nitrites released by alkaline hydrolysis was also monitored to compute nitrogen content and determine nitrocellulose concentration indirectly.

MATERIALS AND METHODS

Several alkaline hydrolysis tests were successively conducted during this investigation. Nitrocellulose was provided by Aqualon, a division of Hercules Incorporated (Wilmington, DE), with approximately 12.2% nitrogen content.

Various doses of sodium hydroxide were used to evaluate the degradation rate of nitrocellulose. Sodium hydroxide solutions were prepared with 0.2%, 0.5%, 1.0%, and 2.0% by weight and were preheated in a water bath prior to their introduction in the reactor. The experiments were carried out in a batch reactor equipped with a mixer and a precision auto temperature controller (Parr Instrument Company, Moline, IL). The experimental set-up is shown schematically in Figure 3.

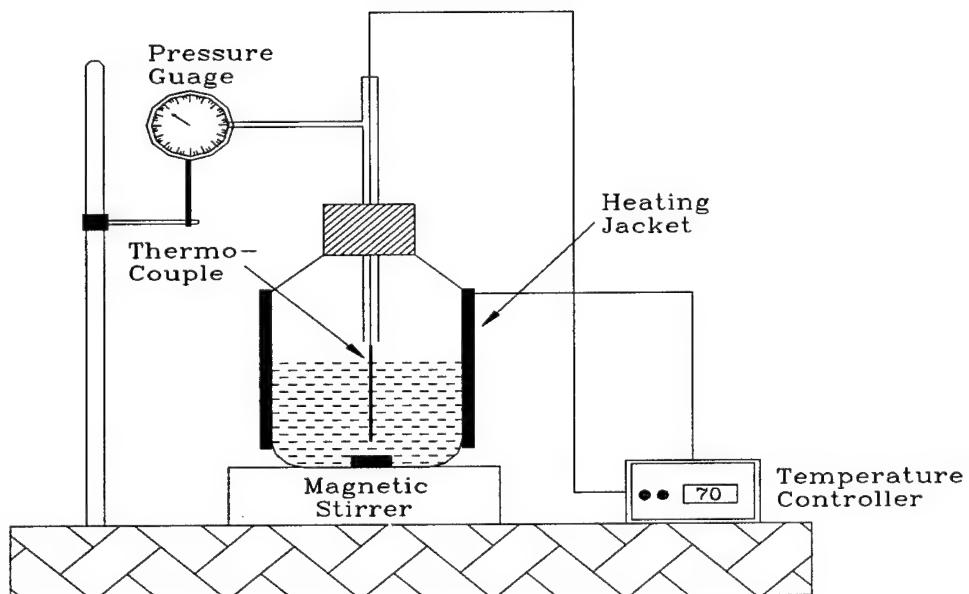


Figure 3: Batch Reactor for Nitrocellulose Hydrolysis

In each batch experiment, approximately 1 gram of nitrocellulose was introduced to the reactor with certain concentration of sodium hydroxide at 70 °C. Concentrations of nitrate, nitrite, and sodium hydroxide and residual of nitrocellulose were monitored every 5 minutes for up to 35 minutes of reaction time. When the time was up at each reaction period, the reactor along with sample were transferred to ice bath to quickly bring temperature down to room temperature. The reactor contents were collected and filtered through a crucible equipped with Whatman 934-AH glass microfiber filter (Whatman Inc., Clifton, NJ) to determine TSS as nitrocellulose residual. Filtrate was collected and nitrate and nitrite concentration were determined by direct injection of filtrate using High Performance Liquid Chromatography (HPLC) on a Varian LC Workstation (Varian, Sugar Land, TX) equipped with a diode array detector, and a Durasep A-1 4.6 mm x 100 mm, 5µm (Alltech Associates Inc., Deerfield, IL) Chromatographic column..

RESULTS AND DISCUSSIONS

Nitrocellulose (NC) decomposition was studied at 70 °C with varying alkali to nitrocellulose ratio. The degree of digestion and the concentrations of nitrite and nitrate were monitored for 35 minutes reaction time at each 5-minute time interval. Typical results of NC hydrolysis are illustrated in Figure 4. Pure NC appears to degrade faster at 2% of NaOH concentration than at 1% or less of NaOH dose. Moreover, 90% of NC digestion was achieved at 2% NaOH dose within 35 minutes. Figure 5 and 6 present nitrate and nitrite nitrogen released during nitrocellulose decomposition. The ratio of nitrite-N to nitrate-N is approximately 2.97 regardless of the degree of digestion. This finding is in good agreement with the results obtained by Kenyon and Gray¹ who found 0.075 mole of nitrite and 0.025 mole of nitrate per liter of alkaline decomposition mixture. Moreover, the independence of this ratio from the degree of digestion suggests that the hydrolysis of nitrocellulose is a single step process where nitrates and nitrites are formed directly from the cleavage of the parent molecules. Wendt and Kaplan⁷ also demonstrated that the decomposition of NC in alkaline environments proceeds in a single step, by determination of the nitrogen, carbon and oxygen contained in the residual (undigested) NC during the course of the reaction.

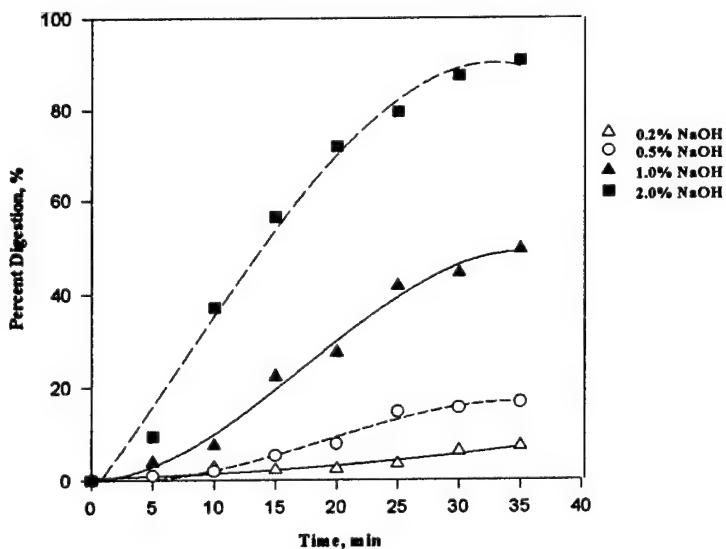


Figure 4: Nitrocellulose Decomposition with Various Sodium Hydroxide Strength

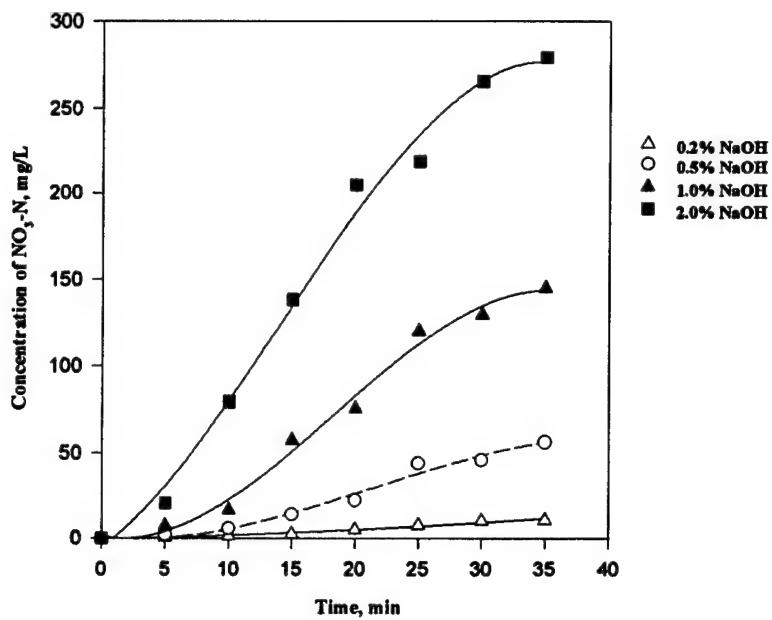


Figure 5: Nitrate-nitrogen Released during NC Decomposition

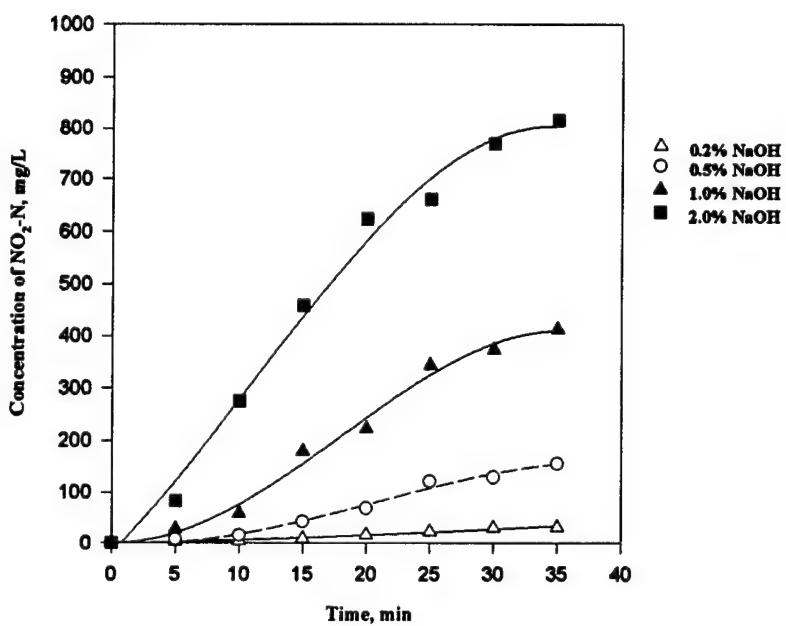


Figure 6: Nitrite-nitrogen Released during NC Decomposition

Preliminary kinetic analysis indicated that the concentration-time history of NC decomposition can be accurately described by a pseudo-first order rate law of the form:

$$\frac{dC}{dt} = -kC$$

where C is the nitrocellulose concentration and k is the first order rate constant. However, the first order rate constant k is a function of NaOH concentration and additional data are required in order to establish its dependence on NaOH concentration.

CONCLUSIONS

The results obtained from this study indicate that alkaline hydrolysis is a viable method for the destruction of nitrocellulose. Alkaline decomposition can be described by a pseudo first order kinetic law but the dependence of the rate constant on the concentration of the alkali must be established at the desired temperature. Nitrogen released during the alkaline digestion is mainly in the form of nitrite and nitrate. The observed ratio of nitrite-N to nitrate-N was approximately 3 and it was independent of the degree of digestion or NaOH concentration.

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AEROBIC BIODEGRADATION OF DI-n-BUTYL PHTHALATE BY PURE AND MIXED BACTERIAL SPECIES

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ABSTRACT

Di-n-butylphthalate (DBP), an organic ester, is primarily used as a plasticizer during the preparation of explosive mixtures. It is abundantly found in the wastewater generated from DBP production plants and munitions manufacturing facilities and at concentrations high enough to create a serious environmental problem. This compound is also listed as a priority pollutant by the USEPA. In this research, the aerobic biodegradation of DBP was studied using several *Pseudomonas* species as well as mixed bacterial cultures in a batch reactor under suspended growth conditions. The work presented in this paper is part of a broader investigation on the biodegradability of gun propellant components. Initial screening experiments, performed in shaker flasks at 30°C on a gyratory shaker rotating at 200 rpm, indicated that *Pseudomonas putida*, *Pseudomonas resinovorans*, and *Pseudomonas cepacia* can all degrade DBP as a sole carbon source. However, *Pseudomonas putida* exhibited higher degradation rates compared to the other two species. In addition to pure bacterial species, mixed cultures obtained from an activated sludge system were found to degrade DBP in the absence of any external carbon sources. A number of batch degradation experiments were performed using different initial concentrations of DBP in order to study the rates of degradation of the compound by *Pseudomonas putida* and activated sludge. The temperature was set at 30°C and the pH was maintained at approximately 7 during the course of the experiment. The higher rate of destruction observed during the kinetic studies suggest that biodegradation is a viable option for the treatment of DBP-containing wastewater.

INTRODUCTION

Di-n-butylphthalate ($C_{16}H_{22}O_4$) is primarily produced by the esterification of phthalic acid using n-butylalcohol in presence of acid or alkali as a catalyst. This compound is being widely used as a plasticizer for the preparation of explosive matrix of double base gun propellant. In addition, it is also being used as cosmetics chemical, diluent in polysulfide dental impression materials, safety glass, printing inks, and adhesives. Due to all these industrial activities, it is abundantly found in industrial as well as municipal wastewater. This compound is characterized as a possible teratogen.¹ The target organs are kidneys,

nerves, and male reproductive system. Thus USEPA listed this compound as a priority pollutant.² An LC₅₀ value of 100 ppb - 1 ppm for larvae of grass shrimp is reported in literature.³

The compound is a colorless oily liquid with a vapor pressure of 0.1 mm of Hg at 115°C and a solubility of 11 mg/L to 4500 mg/L in water listed in different literature.^{3, 4} The higher water solubility poses a serious threat to the environment.

Several technologies are available for treatment of DBP containing propellant formulations such as incineration, chemical treatment, and biological treatment. Incineration would generate some byproducts which could be even more dangerous than the parent compound unless it is done under controlled physical conditions. That would increase the cost of the overall process. Chemical treatment generally require other chemicals and sometimes it also generates other byproducts which have to be treated further. Bioremediation, overcomes these problems at a lower cost. The final products in this treatment process are generally carbon dioxide and water.

Bioremediation is nothing but the use of naturally present microorganisms which use the organic carbon as primary energy source in presence of other inorganic nutrients under aerobic and/or anaerobic environments. This technology has been proved to be cost effective and safe for treatment of several hazardous organic chemicals.

Microbial degradation of DBP was reported in the literature. Wang *et al.* (1995)⁵ found five bacterial strains which can degrade DBP as a sole carbon source. The degradation time was varied from 40 hours to 220 hours for different strains to degrade 100 mg/L of DBP in the suspension. However, the degradation time was reduced when immobilized cells were used. Biotransformation of this compound by *Pseudomonas fluorescens* isolated from subsurface environment was demonstrated by Chauret *et al.* (1995).⁶ The experiments were conducted under aerobic as well as anaerobic conditions. Complete mineralization time was varied from 20 to 70 days in their studies. Wang and Grady (1995)⁷ explored the effects of biosorption and dissolution on the biodegradation of DBP. Biosorption isotherms for DBP by live and dead bacteria was evaluated by Wang and Grady (1994)⁴. Biosorption was significant in both live and dead bacteria, however, it was more in dead bacteria. Pogány *et al.* (1990)⁸ studied metabolism of di-n-butyl phthalate in cell suspension cultures of tomatoes. They found degradation of DBP via a unidentified intermediate to benzoic acid.

In this research, biological treatment of DBP is explored using several pure bacterial species as well as mixed bacterial consortia obtained from an activated sludge plant.

MATERIALS AND METHODS

Analytical Methods

DBP Assay

An HPLC (Varian Instruments Co., Houston, TX) equipped with a tunable detector (Model No. 9065), an autosampler (Model No. 9095), and a pump (Model No. 9010) was used in conjunction with a C8 Beckman Ultrasphere column, C8, 5 μ , 4.6 mm x 25 cm (Alltech Associates Inc., Deerfield, IL) to measure the concentration of DBP. A mobile phase containing 15% water and 85% methanol with a flow rate of 1 ml/min was used to elute DBP and detection was performed at 254 nm. A calibration curve was prepared for DBP upto 100 ppm of DBP concentration and found to be linear within this range. The minimum detection limit was about 1 ppm.

Prior to analysis, aqueous samples from the reactors were centrifuged for 10 minutes at 12,000 rpm in an ultracentrifuge (IEC Centra-M, International Equipment Co.) to separate the biomass. Then, 60 μ l of each sample was injected into the HPLC unit via the auto-sampler.

Biomass Assay

The biomass concentration of the bacterial culture was determined by determining the optical density (OD) measurements. To determine the relationship between optical density and the actual biomass concentration, a calibration curve of optical density versus biomass concentration (mg/L) was prepared. Biomass concentration was determined by measuring the optical density at 540 nm by a diode array spectrophotometer (Hewlett Packard, Model No. 8452). Calibration curves were prepared for both *P. putida* and activated sludge. The procedure followed to develop the calibration curve is described below.

Respective bacterial culture was grown using glucose as the carbon source in a bioreactor. When, the glucose concentration was below detection limit, 100 ml of homogeneous solution was withdrawn from the reactor to determine the total suspended solid. At the same time, optical density of the same solution was measured. This procedure was followed for several dilution of the original liquor. Then the calibration curve was drawn between total suspended solid and optical density.

Organism and Inoculum

All pure cultures used in this study were obtained from the American Type Culture Collection (ATCC). The cultures were stored in a refrigerator at 4°C and transferred when needed. Mixed bacterial consortia or activated sludge was obtained from Linden POTW, Linden, New Jersey.

Growth Media

All growth media and solutions were prepared with deionized water unless mentioned otherwise. The basic composition of growth media was adopted from the ATCC manual. The growth medium used to grow bacteria and activated sludge in all experiments had the composition given in Table 1. The final pH of the solution was between 7.0 to 7.1

TABLE 1: Composition for bacterial growth media

Compound	Amount
Sodium phosphate (Dibasic)	11.2 g
Potassium Phosphate monobasic	5.7 g
Ammonium Sulfate	500 mg
Magnesium Sulfate	100 mg
Manganese Sulfate	10 mg
Ferric Chloride	5 mg
DI Water	1 liter

Experimental Procedures

A number of experiments were conducted to study the biodegradation of DBP. Initial screening experiments were conducted in shaker flasks. Later lab-scale bioreactors were used. The various set-ups and experimental procedures are described in this section.

Shaker Flask Experiment

The purpose of these experiments was to screen and identify various microorganisms to degrade DBP. All shaker flask experiments were conducted in 250 ml Erlenmeyer flasks with a liquid content 100 ml. The

mouths were closed with sterilized tissue paper. An incubator equipped with a gyratory shaker (Gallenkamp, Model # 905) was used for shaking the flasks at 100 rpm. The temperature in the shaker was maintained at 30°C for all the experiments conducted unless otherwise mentioned.

Bioreactor Experiments

A batch reactor (Bioflo II C, New Brunswick Scientific Co., NJ) with a 2.5 liter working volume was used to carry out a number of experiments for the biodegradation of DBP. The reactor was equipped with built in pH, dissolved oxygen and temperature sensors and control systems. The culture was acclimated in the presence of DBP in order to reduce the lag phase. Growth media solution containing certain amount of DBP was placed in the reactor, which was maintained at 30°C, and the solution was inoculated with pure culture or activated sludge. The reactor content was aerated at 2.0 l/min. The pH, DBP, and biomass concentrations were monitored and recorded at specified time intervals.

Desorption Experiments

After the end of each experiment, desorption experiment was conducted to verify any adsorption of DBP on the biomass. The experiment was conducted as follows: 40 ml of suspension was taken from the reactor in a 40 ml vial and centrifuged to separate biomass from the solution. Separated biomass was then mixed with 2 ml methanol and mixed thoroughly for an hour. The solution was then centrifuged again to separate biomass. The clear liquid was taken and injected into HPLC for DBP analysis.

RESULTS AND DISCUSSION

Three aerobic bacteria, namely, *Pseudomonas resinovorans*, *Pseudomonas putida*, and *Pseudomonas cepacia* were tested in order to determine which culture can degrade DBP faster. The results of the preliminary screening for degradation of DBP in shaker flask are shown in Figure 1. For comparison purpose the concentrations were normalized by dividing each concentration by their respective initial concentrations. From Figure 1, it is evident that all three *Pseudomonas* species could degrade DBP within 2 days. However, the degradation rate was faster in case of *P. putida*.

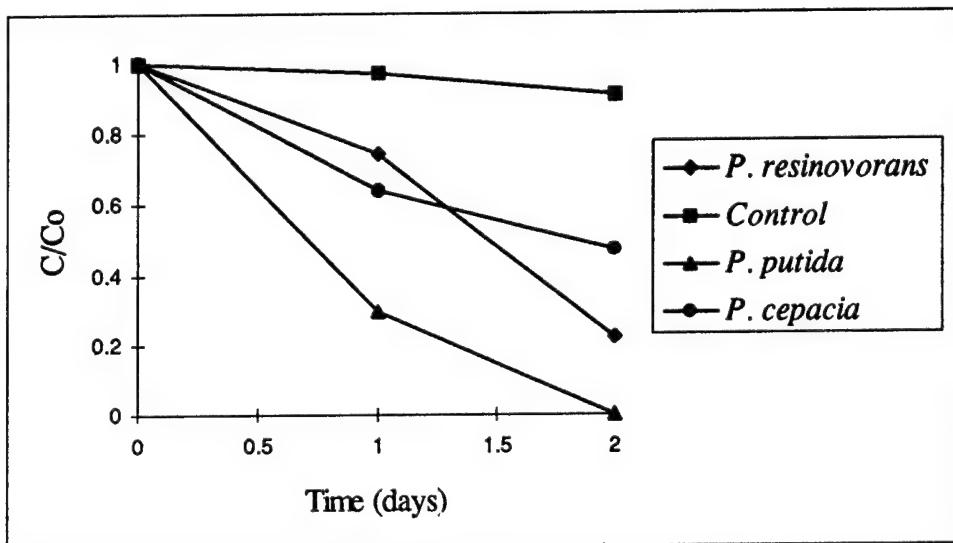


Figure 1. Degradation of DBP by Three *Pseudomonas* species for Screening Purpose

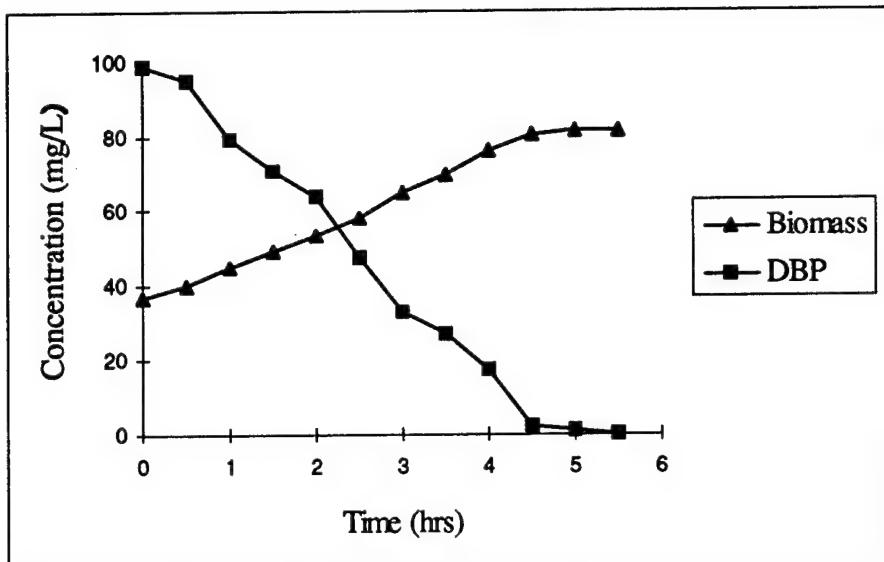


Figure 2. Degradation of DBP by *Pseudomonas putida*

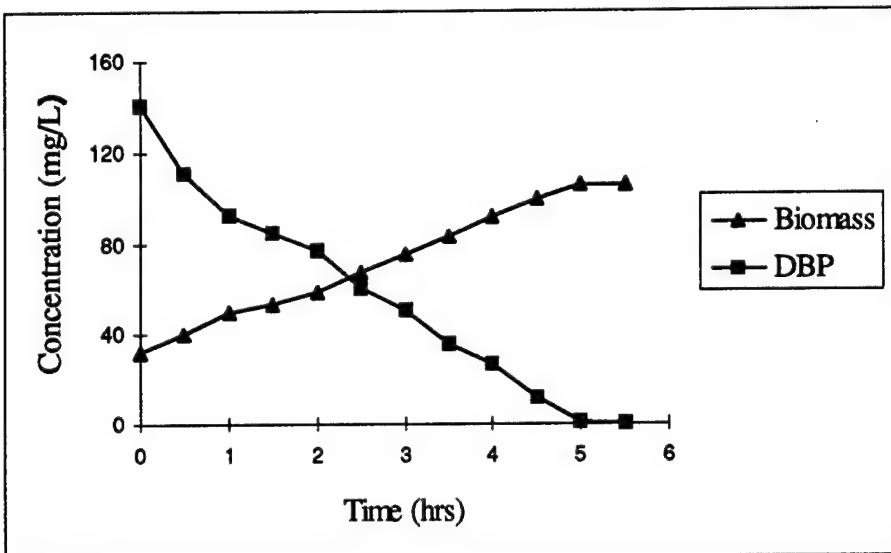


Figure 3. Degradation of DBP by mixed bacterial consortia.

Several experiments were conducted for the degradation of DBP by *P. putida* using different initial concentrations of DBP as well as biomass in a bench scale bioreactor. Initial DBP concentrations were ranged from 14 ppm to 140 ppm in 6 experiments. Typical experimental results are shown in Figure 2. Initial concentrations of DBP and biomass used in this experiment were 98 mg/L and 36 mg/L respectively. DBP and biomass concentration history are shown in Figure 2. It took only about 5.5 hrs to degrade DBP completely. The yield coefficient was about 0.46.

The next experiment was focused on the biodegradation of DBP by mixed microbial consortia in a bioreactor. Initial DBP and biomass concentrations were about 140 mg/L and 30 mg/L respectively. The results are shown in Figure 3. Within 5 hours, complete degradation was observed with yield coefficient of

0.53. The observed yield in this experiment was more than the observed yield by *P. putida* which indicates that mixed microbial consortia can tolerate higher doses of DBP without substantial inhibition.

Finally, the desorption experiment at the end of the degradation study showed that mixed bacterial species exhibited some adsorption of DBP on the biomass. However, with time the adsorbed amount of DBP on biomass decreased with time suggesting that biomass was able to degrade the adsorbed DBP.

CONCLUSIONS

The following conclusions can be drawn for the biodegradation of DBP.

- DBP is a chemical comparatively easy to degrade biologically and can serve as a sole carbon source for various pure and mixed bacterial cultures
- No inhibition was observed upto a concentration of around 140 mg/L for *P. putida* and mixed bacterial consortia.
- The rate of biodegradation by *P. putida* and mixed bacterial consortia were comparatively higher than other pure bacterial cultures.

ACKNOWLEDGMENTS

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MANUSCRIPTS UNAVAILABLE AT TIME OF PUBLICATION

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